IAEA-TECDOC-1663

Radioactive particles in the Environment: Sources, Particle Characterization and Analytical Techniques

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RADIOACTIVE PARTICLES IN THE ENVIRONMENT: SOURCES, PARTICLE CHARACTERIZATION AND ANALYTICAL TECHNIQUES

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FOREWORD

Over the years, radioactive particles have been released to the environment from nuclear weapons testing and nuclear fuel cycle operations. However, measurements of environmental radioactivity and any associated assessments are often based on the average bulk mass or surface concentration, assuming that radionuclides are homogeneously distributed as simple ionic species. It has generally not been recognised that radioactive particles present in the environment often contain a significant fraction of the bulk sample activity, leading to sample heterogeneity problems and false and/or erratic measurement data. Moreover, the inherent differences in the transport and bioavailability of particle bound radionuclides compared with those existing as molecules or ions have largely been ignored in dose assessments. To date, most studies regarding radionuclide behaviour in the soil-plant system have dealt with soluble forms of radionuclides. When radionuclides are deposited in a less mobile form, or in case of a superposition of different physico-chemical forms, the behaviour of radionuclides becomes much more complicated and extra efforts are required to provide information about environmental status and behaviour of radioactive particles. There are currently no documents or international guides covering this aspect of environmental impact assessments.

To fill this gap, between 2001 and 2008 the IAEA performed a Coordinated Research Programme (CRP- G4.10.03) on the 'Radiochemical, Chemical and Physical Characterization of Radioactive Particles in the Environment' with the objective of development, adoption and application of standardized analytical techniques for the comprehensive study of radioactive particles. The CRP was in line with the IAEA project intended to assist the Member States in building capacity for improving environmental assessments and for management of sites contaminated with radioactive particles.

This IAEA-TECDOC presents the findings and achievements of the above CRP in the area of measurement and characterisation of radioactive particles in the environment. Ten IAEA Member States, namely Denmark, Finland, Hungary, Israel, Kazakhstan, Norway, Russian Federation, Spain, Ukraine, the UK, the USA and the EC Institute of Transuranium Elements (ITU) participated in the CRP.

The IAEA acknowledges to contributions of all the participants and mentoring by Prof. Brit Salbu. The IAEA also wishes to express its gratitude to N. Vajda for her kind assistance in editing and preparating this publication for publishing, as well as to all the contributors to the IAEA-TECDOC and those who assisted in its drafting and review. The IAEA officer responsible for this publication was S. Fesenko of the Department of Nuclear Sciences and Applications, IAEA Environment Laboratories.

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1. INTRODUCTION

1.1. BACKGROUND

Measurements of environmental radioactivity and any associated assessments are often based on the average bulk mass or surface concentration, and assume that radionuclides are homogeneously distributed as simple atomic species. However, effluents released from nuclear reactors, fuel fabrication facilities, and/or reprocessing plants under normal operating conditions are known to contain radionuclides in different chemical and physical forms. Similarly, a significant fraction of radionuclides released by nuclear events, such as testing of nuclear weapons, nuclear reactor accidents, and other activities involving nuclear installations, are in the form of radioactive particles (RP) of various size, composition and specific activity, and/or associated with aerosols, colloids or other complexes. It is generally not recognized that a significant fraction of the bulk sample activity is due to the heterogenic distribution of radioactive particles present in the environment, thus leading to sample heterogeneity problems, and false and/or erratic measurement data.

Moreover, the inherent differences in the transport and bioavailability of particle bound radionuclides compared with those existing as molecules, ions, or complexes have largely been ignored in radiation dosimetry and risk estimates. As a result, there is a high degree of scientific uncertainty about the levels of risk to human health and the long-term ecological consequences of radioactive particles present in the environment. For example, inadequate transport and dosimetry models are used for characterizing the resuspension and intake by inhalation of high specific activity particles and the associated local internal doses. Research is clearly needed to address these concerns, and to provide fundamental data and information on the different physical forms, size and frequency distribution, transport and behaviour of radioactive particles on which sound environmental assessments can be made.

In 2001, no standard techniques were available for the collection, isolation and measurement of radioactive particles in the environment. Little or no information was available on the source-specific properties of radioactive particles nor was there adequate background data on the distribution, transport and bioavailability of particle bound radionuclides to fully describe associated dose/risk distributions. This information is needed to evaluate the correlation between chemical, structural and transport properties of particles formed under different release conditions, and the ultimate fate and interaction of particle bound radionuclides within the biosphere. It was expected that the CRP research would contribute to building a stronger scientific basis for environmental assessments at contaminated sites worldwide, help to develop more appropriate methods and criteria for remediation, and provide for more accurate dose/risk estimates.

Radioactive particles are defined as a localized aggregation of radioactive atoms that give rise to an inhomogeneous distribution of radionuclides significantly different from that of the matrix background. In water, particles are defined as entities having diameters larger than 0.45 μm, i.e. that will settle due to gravity. Radionuclide species within the molecular mass range 0.001 μm - 0.45 μm are referred to as radioactive colloids or pseudo-colloids. Using the grain size categories for sand, silt and clays, particles larger than 2 mm should be referred to as fragments. In air, radioactive particles ranging from submicron in aerosols to fragments are classified according to the aerodynamic diameters, where particles less than 10 μm are considered respiratory. Thus, radionuclides released to the environment are known to occur in any of the following phases:

- Fuel particles or particles of fissile material formed by mechanical disruption, pulverisation and dispersion of the original bulk of radioactive material, ranging in size from submicron to fragments (e.g. U or Pu particles);

- Condensed aggregates or molecular particles, and particles formed upon condensation of volatile radionuclides;

- Discrete radioactive particles or clusters formed within the fuel during normal operations or during the release (e.g. Ru particles);

- Colloids and/or pseudocolloids (e.g. 1–450 nm) either released directly or formed in the environment;

- Low molecular mass species <1 nm having a nominal molecular mass less than 1 kDa (e.g. simple ions, complexes, chelates).

Based on research performed within the framework of the CRP and literature data related to former nuclear weapons test sites or sites associated with nuclear accidents, it could be concluded that a significant fraction of the distributed radioactive material remains localized in the form of discrete particles of various size, composition and structure long after its release.

Fuel and condensed radioactive particles were released into the environment as a result of atmospheric nuclear weapon tests conducted at a number of different sites world-wide, e.g. Bikini and Enewetak Atolls (Marshall Islands), Maralinga (Australia), Mururoa (French Polynesia), Nevada test site (USA), and Semipalatinsk (Kazakhstan), as detailed in Section 4. Other nuclear tests, in particular the so-called safety tests, where conventional explosives were used and little or no fission energy was released, dispersed up to millimetre sized particles containing Pu and other actinide elements into the environment.

Following high temperature accident scenarios (e.g. the Chernobyl accident), a range of different U fuel particles and condensed particles varying in composition, structure, and oxidation state were observed. Following low temperatures releases (e.g. pre 1957 Windscale releases), flake-like U fuel particles significantly different from those collected at Chernobyl accident affected areas were identified. Radioactive particle releases have also occurred at the Rocky Flats nuclear installations (USA) and the Windscale facility (UK) as a result of incidents involving fires. Accidents involving nuclear weapons near Thule (Greenland) and Palomares (Spain), and the failure of Cosmos 954 satellite have all led to the dispersion of significant quantities of particulate forms of Pu into the environment. Radioactive particles have also been identified in the fjords of Novaya Zemlya (Russian Federation) in close vicinity to radioactive waste dump sites. Furthermore, a major fraction of radionuclides released in effluents from reactors and reprocessing plants (Sellafield, UK; La Hague, France) are in the form of particles and colloidal material. Clearly, there are a large number of source-specific releases around the globe that contained high specific activity particles and/or other discrete entities that we define here globally as radioactive particles. Therefore, increased understanding of the relative distributions, transport and ultimate fate of particle bound radionuclides is essential to reduce the uncertainties associated with assessments of the radiological situation at these sites.

After their release, radioactive particles represent point sources of potential long-term environmental and ecological significance. As these materials may include high specific activity isotopes there is a human exposure risk due to inhalation, dermal absorption, wound exposure and ingestion of the particles. Additionally, particles may be retained by filter-feeders (e.g. molluscs) and eventually be ingested by man. Furthermore, weathering of radioactive particles will increase the mobility and potential for incorporation of particle bound radionuclides into the biosphere. Radiological assessments based on average bulk mass or surface activity concentrations will therefore be biased depending on the assumptions made. Weathering rates will depend on particle composition (e.g. UO_2 fuel), on structural changes occurring during the event (e.g. transformation from UO_2 to U_3O_8), and on local chemical conditions and transformation processes occurring after deposition (e.g. pH, redox conditions, bioerosion). These processes will be particularly important in controlling remobilisation of mobile radionuclides such as ^{90}Sr. Thus, information on key chemical, physical and transport properties of radioactive particles could be used to help facilitate environmental management of contaminated sites. For example, knowledge related to particle size, solubility and transport of particles may influence the evaluation of human health risks for different types of exposures, and provide a scientific basis for developing new cleanup standards and associated technologies.

The CRP recognized the importance of the contribution of radioactive particles to human health and ecological impacts of radionuclides released into the environment from a wide range of different sources. The studies included in the CRP have also highlighted common problems related to analytical measurements and sample homogeneity, incomplete dissolution of samples, and potential differences in the transport, solubility and dosimetric properties of particle-associated radionuclides compared with those existing as atoms, molecules, ions or complexes. As a consequence of these problems, there has been a lack of knowledge and high degree of uncertainty about the short- and long-term health and ecological impacts of particle associated radionuclides. Moreover, there has been a lack of standard techniques and valid reference materials for the collection, isolation and analysis of radioactive particles. Therefore, research was needed at an international level to develop and standardize appropriate methodologies, and assemble and disseminate available measurement data on the size, structure and composition of radioactive particles from different source terms and under different release conditions.

This IAEA-TECDOC (hereafter referred to as the ‘Report’) is primarily intended to provide the Member States with an overview of different types of radioactive particles released to the environment, their characteristics and the analytical techniques that can be applied for the characterization of the particles; to provide guidance on the application of such techniques with detailed references and to reveal advantages and drawbacks, failures, difficulties, inconsistencies of the different techniques; and to highlight up-to-date solutions and methods that could widen our knowledge about radioactive particles. The Report is also intended for use in the updating of other IAEA documents related to the assessment of the radiological impact of radioactive discharges and can be also used as background documentation for other relevant activities such as training in application of radio-, nuclear and micro- analytical techniques.

1.2. OBJECTIVES

The major objectives of this document are to give an overview on the micro- and radioanalytical techniques which could be applied for characterization of radioactive particles and to provide guidance for application of the techniques for evaluation of contaminated areas. The specific objectives of the document are the following:

1. To gain recognition of the importance of radioactive particles in environmental contamination.
2. To propose standardized techniques to characterize key physical and chemical properties of radioactive particles and colloids.
3. To establish a set of standards to describe key properties of radioactive particles as a function of different source terms and/or release scenarios.
4. To suggest standardized techniques for collection and determination of key physical and chemical properties of radioactive particles and colloids.
5. To improve understanding of the role played by radioactive particles in environmental contamination issues.

1.3. SCOPE

The Report covers present knowledge on nuclear sources that can contribute to the release of radioactive particles into the environment over the years, source-specific information on radioactive particles and applicable analytical techniques.

1.4. STRUCTURE

This Report consists of 5 sections. The main sources of radioactive particles in the environment, such as different nuclear fuel cycle activities (including radiation accidents), nuclear weapon testing, dumping of radioactive waste and accidents involving nuclear weapons and satellites, are described in

Section 2. Section 3 is devoted to analytical techniques to study radioactive particles, considering (i) identification of radioactive particles in the environment and (ii) their isolation from environmental samples, (iii) micro-manipulation and micro-surgery of particles prior to analysis, and (iv) application of nuclear analytical techniques for characterisation of radioactive particles. Section 4 provides the results of worldwide studies on characterisation of radioactive particles from different sources based on the application of the techniques described in Section 3. Results from CRP activities on radioactive particle characterisation in different areas are also given in Section 4, while a summary and recommendations from the CRP are given in Section 5.

2. SOURCES OF RADIOACTIVE PARTICLES IN THE ENVIRONMENT

Parallel to the fast development of the nuclear industry and the widespread use of radioactive isotopes, radioactive material has been released to the environment from various sources as a result of actions committed either on purpose or accidentally through negligence or simply ignorance. Regarding the global radiological consequences, expressed as collective effective dose to the public, the major contributors to environmental contamination were the nuclear weapons tests followed by the accidents of the nuclear fuel cycle. The 2000 UNSCEAR report [1] gives an estimation of the total amount of radioactive materials released to the environment and their distribution due to atmospheric nuclear testing, and due to reactor and reprocessing plant operations.

2.1. NUCLEAR WEAPONS TESTS

The largest source of global radiological contamination was atmospheric testing of more than 500 nuclear weapons at Semipalatinsk in Kazakhstan, on Novaya Zemlya in Russian Federation, at the Nevada test site in the USA, in the Marshall Islands, on Lop Nor in China, on the Atolls of Mururoa and Fangataufa used by the French and on the Maralinga and Emu sites in Australia (used by the UK) [1–9]. At most of these grounds, atmospheric as well as underground tests as well as so called safety trials were performed. The latter ones produced little or no nuclear yield, but dispersed Pu or ^{235}U with conventional explosives. Furthermore, nuclear detonations were used for civil purposes (PNE; peaceful nuclear explosions). Although inventory data about explosion tests are scarce and often kept confidential, some publications and reports issued recently have revealed information about the number of weapons exploded and the environmental situation at the former test sites or more often at their surroundings.

Nuclear weapons tests and nuclear device explosions were carried out in the former Soviet Union between 1949 and 1990. In addition to the 715 nuclear weapons tests for military purposes, so called peaceful nuclear explosions were conducted from 1965 to 1990, resulting altogether in 969 explosions including near surface, atmospheric, underwater and underground explosions. The majority of the nuclear tests were conducted at two major test sites, namely, the Semipalatinsk and the Novaya Zemlya sites [2, 3].

From 1949 to 1989, about 456 atmospheric and underground nuclear test explosions were conducted in the region near Semipalatinsk City, in Kazakhstan. At the Semipalatinsk test site, the first nuclear bomb in the USSR was detonated in 1949, and the first hydrogen bomb was detonated in 1953. High levels of ^{239,240}Pu contamination (30 kBq kg^{-1}) have been reported at the first experimental site, which was used until 1962. Transuranium ratios differed from one site to the other indicating that different types of weapons have been tested. An environmental monitoring program involving various organizations was carried out in 1991–1993, and the IAEA conducted environmental surveys around Semipalatinsk in 1995.

In the Northern test site of the USSR, at Novaya Zemlya Island, about 140 nuclear test explosions were conducted during from the 1950s to 1990 [1, 2]. Significant contamination of actinides and fission products has been localized to the 3 major test areas on the island. The contamination has been attributed to some major events: radioactive plumes from underwater tests in Chernaya Bay (1955, 1957, 1961), radioactive plumes from surface tests at Chernaya Bay (1957 and 1961), fallout from the low altitude atmospheric explosions in 1957, and dumping in the Chernaya Bay in 1991 [2, 3]. Additional nuclear explosions (military and PNEs) have been conducted in different parts of the former Soviet Union, including missile testing in the atmosphere, atmospheric nuclear explosions near Totsk (Orenburg, Russian Federation) and near surface explosions near Aral'sk (Kazakhstan). Information on particles released at Novaya Zemlya or from the areas affected by PNEs is scarce. Joint Russian-Norwegian expeditions to the Kara Sea and to the dumping sites in the fjords of Novaya Zemlya were performed in 1992–1994.

From 1951 to 1962, 84 atmospheric tests and more than 900 underground weapons tests were performed at the Nevada test site, in the United States [1, 4, 8]. Venting took place during 32 of the underground tests. In addition, 31 nuclear rockets and 6 ramjets were tested at the site, with minor releases of activity.

Between 1946 and 1958, a total of 23 atmospheric nuclear tests were conducted by the United States at Rongelap and Bikini Atolls on the Marshall Islands, including large-scale thermonuclear bomb tests. In 1969, a general cleanup of debris was started. After a preliminary radiological survey in 1970, people returned to Bikini Atoll. In 1978, they had to be relocated again because of high doses [4]. The IAEA conducted environmental surveys on the Bikini Islands in 1997.

Mururoa Atoll, in French Polynesia, was used for atmospheric testing between 1966 and 1974 and underground testing from 1976 to 1996 by the French government. The first three experiments were made on barges, a few metres above the lagoon; thus the fireball interacted with the lagoon bottom. In the subsequent experiments the nuclear devices were suspended from a balloon. During the atmospheric testing period, the atoll was also used to conduct safety experiments on the coral bedrock [5]. After each safety experiment the Pu deposits were removed or fixed with bitumen. The IAEA conducted environmental surveys on Mururoa and Fangataufa in 1996.

At Maralinga and Emu in South Australia, the UK conducted a program of nuclear weapons trials between 1953 and 1963. Nine major and several hundred smaller scale experiments were performed, the largest nuclear detonations having yields of 1 and 27 kilotons. Between 1960 and 1963, 12 hydronuclear and single point safety trials were also carried out in which 22 kg of Pu and about the same amount of ^{235}U were dispersed [6, 7, 8]. Clean-up campaigns took place on the most contaminated area of Taranaki in 1964 and 1967. A major environmental survey was conducted in 1984.

Smaller bombs of several kilotons explosion yield caused local or regional contamination, because the radionuclides that were dispersed into the troposphere and not the higher layers of the atmosphere. Nuclear bombs with explosion yields equivalent to megatons of TNT released radionuclides high into the stratosphere, and the debris circled the earth a number of times resulting in worldwide fallout.

A total non-local fission explosion yield of 155 Mt was assumed based on the measured ^{90}Sr deposition [1]. An estimate of the total radioactivity, by nuclide, released into the atmosphere by above-ground tests is about 2.5×10^{21} Bq (not including noble gases and very short-lived nuclides). Table 1 lists the distribution of the total radioactivity among the isotopes.

It is estimated that about 3500 kg of Pu isotopes were distributed on the earth's surface due to atmospheric nuclear weapons tests and another 100 kg was released in underground tests. This value corresponds to a release of about 13×10^{15} Bq of ^{239}Pu and ^{240}Pu [1].

Radioactive particles are expected to be found at the weapons test sites and in their surroundings as a result of local and regional fallout. Radioactive particles have been collected from all the above-mentioned sites except for Novaya Zemlya, despite the remedial actions that were performed at some of these sites.

Excluding volatile nuclides such as noble gases, tritium, ^{14}C, ^{131}I and ^{137}Cs, the activity attributed to particulate material – although an exact number has not been defined – should be a substantial portion of the total activity.

TABLE 1. RADIONUCLIDES PRODUCED AND GLOBALLY DISPERSED IN ATMOSPHERIC NUCLEAR TESTING [1]

Radionuclide	Half-life	Global release (10^{18} Bq)
^{3}H	12.33 a	186
^{14}C	5730 a	0.213
^{54}Mn	312.2 d	3.98
^{55}Fe	2.73 a	1.53
^{89}Sr	50.6 d	117
^{90}Sr	28.5 a	0.622
^{91}Y	58.5 d	120
^{95}Zr	64.0 d	148
^{103}Ru	39.25 d	247
^{106}Ru	365 d	12.2
^{125}Sb	2.73 a	0.741
^{131}I	8.04 d	675
^{137}Cs	30.0 a	0.948
^{140}Ba	12.75 d	759
^{141}Ce	32.5 d	263
^{144}Ce	285 d	30.7
^{239}Pu	24110 a	0.0065
^{240}Pu	6560 a	0.0044
^{241}Pu	14.4 a	0.142

2.2. NUCLEAR FUEL CYCLE

Releases of radioactive materials into the environment occur in each part of the nuclear fuel cycle from mining and milling through fuel fabrication, reactor operation and reprocessing of spent fuel to the end of cycle operations as waste management [10]. To show the relative radiobiological significance of the various activities of the fuel cycle, Table 2 compares the estimated collective effective dose to the public from different radionuclide sources according to the UNSCEAR 2000 report [1].

According to the recent estimates in the UNSCEAR 2000 report [1], the greatest contributor to the public dose is radioactive waste disposal activities. The significance of mining and milling activites has been re-evaluated due to newer, more environmentally friendly technologies, and to modifications in dose calculation methods. Nonetheless, U mining and ore processing have contaminated many areas that have been or are being remediated, while others still require remediation.

2.2.1. **Accidental releases from nuclear reactors**

In this section, the major accidents involving discharges of enhanced amounts of radionuclides from nuclear reactors and reprocessing plants are discussed. Some figures are given about the unavoidable controlled releases during normal operation of the facilities.

TABLE 2. COLLECTIVE EFFECTIVE DOSE TO MEMBERS OF THE PUBLIC FROM RADIONUCLIDES RELEASED IN EFFLUENTS FROM THE NUCLEAR FUEL CYCLE (Adapted from UNSCEAR report 2000 [1])

Source	Normalized collective effective dose (manSv/GW$_e$a)	
	Local and regional effects	1995-1997
Mining		0.19
Milling		0.008
Mine and mill tailings (releases over 5 years)		0.04
Fuel fabrication		0.003
Reactor operation		
Atmospheric		0.4
Aquatic		0.04
Reprocessing		
Atmospheric		0.04
Aquatic		0.09
Transportation		<0.1
Total (rounded)		0.91
	Solid waste disposal and global effects	
Mine and mill tailings		
releases of radon over 10 000 a		7.5
Reactor operation		
low level waste disposal		0.00005
Intermediate-level waste disposal		0.5
Reprocessing solid waste disposal		0.05
Globally dispersed radionuclides (truncated to 10 000 a)		40
Total (rounded)		50

On April 26, 1986, a low power engineering experiment was being conducted at the 4th reactor unit of the Chernobyl nuclear power plant (NPP) in the Ukraine. The reactor became unstable, resulting in a nuclear excursion, thermal explosions and fires. During the reactor accident, about 4 × 10^{18} Bq of radioactive U fuel were released over a period of ten days, until the fire was extinguished and the damaged reactor entombed in concrete. The majority of the radioactive material was dispersed in western and northern directions. Table 3 shows the distribution of the principal radionuclides released to the environment from this accident [1].

A comparison of the activities of the released components with the core inventory [9] shows that about 3% of the non-volatile core components were ejected into the environment. Radioactive substances were released from the reactor in the form of particles ranging from submicrons to fragments, with the exception of noble gases and some iodine nuclides which were volatilized. The total mass of released radioactive material was about 6000–8000 kg. The total amount of inactive material interacting with the fuel components and influencing the release and transport properties of radioactive material was probably much larger. Environmental survey programs and clean-up of the debris were started soon after the accident. A series of investigations have demonstrated that radioactive particles were released during the explosions and during the subsequent fires [11–15]; conclusions of these investigations will be briefly presented in Part II of this report.

TABLE 3. PRINCIPAL RADIONUCLIDES RELEASED INTO THE ENVIRONMENT FROM THE CHERNOBYL ACCIDENT (Adapted rom UNSCEAR report 2000 [1])

Radionuclide	Half-life	Estimated release (10^{18} Bq)
^{85}Kr	10.72 a	0.033
^{89}Sr	50.5 d	0.115
^{90}Sr	29.12 a	0.01
^{95}Zr	64.0 d	0.084*
^{103}Ru	39.3 d	0.168
^{106}Ru	368 d	0.073
^{131}I	8.04 d	1.760
^{133}Xe	5.25 d	6.5
^{134}Cs	2.06 a	0.047*
^{137}Cs	30.0 a	0.085
^{140}Ba	12.7 d	0.24
^{141}Ce	32.5 d	0.084*
^{144}Ce	284 d	0.050*
^{239}Np	2.36 d	0.400
^{238}Pu	87.74 a	0.000015*
^{239}Pu	24065 a	0.000013*
^{240}Pu	6537 a	0.000018*
Total release (excluding noble gases)		~7*

* Updated data from 'Environmental Consequences of the Chernobyl Accident and their Remediation: Twenty Years of Experience'. Report from the Chernobyl Forum Expert Group 'Environment', IAEA 2006.

Besides the global scale Chernobyl accident, other reactor accidents have contributed to environmental contamination on a regional scale.

From 1952 to 1957, particles of U oxide containing fission products were inadvertently discharged from the stacks of two air-cooled, graphite moderated natural U metal fuelled reactors at Windscale, UK. Cartridges of irradiated fuel were misplaced in the outlet air ducts, where the U became oxidized and particles of U oxides were dispersed via the stacks [11]. It is estimated that about 20 kg of U fuel in the form of particles were released during this period. A different type of release occurred during a graphite fire in the core of Pile 1 in October 1957, where radioactive particulate matter was released and part of the plume reached Scandinavia. Due to the graphite fire, about 10^9 Bq of ^{239}Pu were released, probably associated with U oxide particles [16].

The core melt down accident at the Three Mile Island (TMI) Reactor in the United States happened on March 28, 1979. The estimated total atmospheric release in the TMI accident was 10^{12} Bq, i.e. six orders of magnitude lower than in the Chernobyl accident [10]. Due to proper containment, no particulate material was released, but volatiles such as noble gases were detected outside the facility.

2.2.2. Releases from nuclear reactors under normal operation

During normal operation of nuclear reactors, radionuclides are released through atmospheric and aquatic pathways, and routinely monitored by nuclear safeguard inspections. The major constituents of the releases are noble gases, tritium, ^{14}C and iodine, all of them gases or volatile elements. Particulate materials represent small amounts of the total activity in the effluents (less than 0.001%). The total activities and the effective doses to the public from the two effluent streams are quite insignificant. According to the UNSCEAR 2000 report [1], global releases of radionuclides by reactors up to 1997 are responsible for a collective effective dose to the public of approximately 2900 man-Sv.

Nuclear fuel particles are rarely detected in the effluents during normal operating conditions of the nuclear power plants, although they have been identified in releases from Swedish power reactors [17]. Nonetheless, particles from failed fuel pins can be released into the coolant which can transport them to various parts of the power plant. More often activated metallic particles or corrosion particles are released to the coolant and transported in the primary circuit and occasionally outside the circuit.

2.2.3. Releases from reprocessing plants

Reprocessing plants were major sources of environmental contamination in the past history of Pu production, when radioactive waste solutions were often discharged directly into rivers or into the sea. In addition to the continuous releases, occasional accidental releases have occurred over the years. In the last decades, many safety measures were introduced to improve reprocessing, and the current releases in normal operating conditions are at levels that should not be of concern. Until the mid-1990s, the liquid effluents from reprocessing plants were responsible for the major part of the global collective dose commitment of nuclear power generation, i.e. for about 4700 man-Sv relative to the 2900 man-Sv commitments due to nuclear reactor operation [1]. However, by the end of the nineties, the ratio of the releases from fuel reprocessing and from reactor operation had changed completely: in 1995–1997 about 320 man-Sv originated from reactor operation, while only 100 man-Sv was attributed to fuel reprocessing.

The Mayak PA, located in the southern Urals, Russian Federation and connected to the Ob River system, was the first weapon production facility in the USSR. Between 1949 and 1951 about 76 million cubic metres of liquid radioactive waste with a total activity of 1.0×10^{17} Bq were released into the Techa river, which is linked to the Arctic Sea through the rivers Iset, Irtysh and Ob [2, 18]. About 2.5 million cubic metres of waste corresponding to 4.4×10^{18} Bq were also released into Lake Karachai near the Mayak PA. Due to a severe drought in 1967 the lake water level decreased and radioactive sediments of about 20×10^{12} Bq activity were dispersed into the environment by a tornado. High-level liquid radioactive waste is stored in surface tanks at the Mayak PA site. In 1957 one tank exploded due to insufficient cooling. The liquid sludge was ejected to a height of 2 km and approximately $74–740 \times 10^{15}$ Bq radioactive material was spread into the environment, resulting in contamination of approximately 15000–23000 km^2 of land [2].

Similarly, radioactive contamination of the River Tom, a tributary to the River Ob, occurred due to direct releases from the Siberian Chemical Combine at Seversk (Tomsk-7). Radioactive materials were also accidentally released from the reprocessing plant in the Tomsk-7 military complex, Russian Federation in 1993 [2, 3]. A process tank containing a U-Pu solution exploded and radioactive solution was ejected into the environment. Hot spots were detected in the soil [3]. Due to direct effluents from Krasnoyarsk Mining and Chemical Combine (Facility), Zheleznogorsk (Krasnoyarsk-26) into the River Yenisey, severe contamination including the presence of radioactive particles is documented [2, 3].

Severe contamination occurred in the USA within its nuclear weapons complex [9]. Hanford was the first industrial-scale Pu production site. Between 1944 and 1981, approximately 220 000 cubic metres of liquid reprocessing waste, totalling 11.8×10^{18} Bq, were produced and stored. Up to 3800 cubic metres were released into the environment. During the earlier period of operation, some high level wastes and contaminated liquids were discharged directly into the ground thus contaminating approximately 500 km^2 of land. In Oak Ridge, 160 000 cubic metres of liquid waste containing fission products and transuranium elements were directly discharged into the ground creating a radioactive burden of about 44×10^{12} Bq.

Of the 3 major reprocessing plants in Europe (Sellafield and Dounreay, UK, La Hague, France), the British nuclear fuel reprocessing plant Sellafield has been the greatest contributor of actinides to the North European seas [19]. At Sellafield, discharges into the Irish Sea amounted to about 1.3×10^{15} Bq between 1950 and 1992, including significant amounts of transuranium nuclides, i.e. 0.72×10^{15} Bq of plutonium (^{238}Pu, ^{239}Pu, ^{240}Pu). According to other sources, in acceptable agreement with the above-mentioned data, about 37×10^{12} Bq of Pu had been released yearly into the sea. In comparison, the

Dounreay and La Hague facilities released respectively 0.5% and 1.5% of the amount of alpha emitters released by Sellafield [19]. Radioactive particles have been identified in the surroundings of Dounreay and Sellafield, partly due to former accidental releases. The sediments in the Irish Sea, especially outside the pipeline, act as a sink and are highly contaminated partly due to sedimentation of particles. Due to remobilization of Pu, however, contaminated sediments act as a diffuse source. Speciation studies of the Sellafield and La Hague effluents demonstrated that a major fraction of the radionuclides were released as particles and colloids. The Sellafield and La Hague effluents were differentiated using transmission electron microscopy [20], showing that Sellafield-derived Pu is being transported out of the Irish Sea towards the Norwegian coast.

Thus, it is very likely that the major fraction of refractory transuranium nuclides released from reprocessing plants is present as radioactive particles or colloidal material. Remobilisation of particle associated radionuclides from contaminated sediments may be occurring or may occur in the future.

2.3. OTHER SOURCES OF RADIOACTIVE PARTICLES

Accidents involving nuclear weapons and satellites using transuranium elements as power sources have led to the dispersion of radionuclides into the environment. In 1966, a US Air Force B-52G bomber carrying four 1.5 Mt thermonuclear bombs collided with a fuel tanker aircraft during a refuelling operation over Palomares, Southern Spain, triggering an explosion and fire at an altitude of 8500 m. The B-52G broke apart, one of the thermonuclear bombs fell in the ocean and the other three fell on land. The conventional explosives from two of the bombs that fell on land detonated without setting off a nuclear explosion. This ignited the plutonium they contained, producing a cloud that was dispersed over an area of 2.3 km^2 close to Palomares. Mixed Pu and U particles have been identified [21] in the area.

In 1968, a B-52 bomber carrying four thermonuclear bombs caught fire and crashed on the ice at Thule, Greenland [22]. Due to explosion and fire, particles containing Pu and U were dispersed within a distance of few kilometres and some of the fissile material was located in the sediment of the Bylot Sound [22].

Additional releases occurred upon re-entry of satellites powered by nuclear sources. About 0.6×10^{15} Bq of ^{238}Pu were released over the south Pacific in the high altitude destruction of the SNAP-9 satellite power source in 1964 [1]. The Soviet nuclear powered satellite Cosmos 954 re-entered the atmosphere in 1978 and crashed in the Northwest Territories in Canada. About one quarter of the reactor core, mainly in the form of particles and fragments of different sizes, was recovered. It is expected that the rest of the core remained in the upper atmosphere as fine dust particles, contributing to global fallout. More than 4000 (sub)millimetre-sized particles up to several MBq activity were detected in the surrounding environment [2].

Other contamination sources are nuclear submarines and other dumped radioactive objects. The fjords of Novaya Zemlya, Russian Federation were used as dumping sites for radioactive wastes. Three reactors with spent fuel, five reactors without fuel, four vessels and numerous containers were dumped in the Abrosimov fjord since 1965. In the Stepovogo fjord, a submarine with two fuelled reactors was dumped in 1981 and several containers were also located. In the Tsivolky fjord, reactors without fuel and containers were dumped, and in 1972, a fuelled reactor from a submarine was dumped in the open Kara Sea. The fuel assemblies from the icebreaker ‘Lenin’ were lost during transport and have still not been located. Russian-Norwegian expeditions to the area took place in 1992–1994 to reveal the environmental situation. Although leakages were observed and other sources contributed to the radioactive contamination, the radiological impact to man was low. During the expeditions, ^{60}Co containing radioactive particles were identified in the sediment [2, 23].

Depleted uranium (DU) is the by-product of the production of enriched uranium. Due to its high density, DU is used for military and civil purposes, e.g. in ammunition or as counterweights in aircrafts, as radiation shielding, and as chemical catalysts. DU ammunitions were used during the Gulf war in Kuwait, the civil wars in Bosnia-Herzegovina and also in Kosovo. Fine particles of DU were dispersed into the environment and contaminated the battle fields [24, 25].

3. ANALYTICAL TECHNIQUES TO STUDY RADIOACTIVE PARTICLES

3.1. IDENTIFICATION AND ISOLATION OF RADIOACTIVE PARTICLES

Key particle characteristics influencing mobility and ecosystem transfer, biological uptake and effects include particle size distributions, surface and bulk (3D) elemental composition, structure and morphology, oxidation state and weathering rates [12]. Due to their small sizes, often in the range few micrometres, radioactive particles are difficult to locate, identify and characterize. It is likely that the lack of a reliable procedure for their identification often leads to negligence of radioactive particles and underestimation of the role they play in environmental contamination. Information on how to locate, identify and further isolate particles has been very scarce, and new techniques became available only recently.

3.1.1. Identification of the presence of radioactive particles

The usual identification procedure consists of in-field monitoring of anomalously high radioactivity (hot spots), sampling of bulk material, preparation of thin layers by filtering aerosols or solutions or spreading solid material on sheets, and finally analysis of the layers to determine the activity distribution.

For any sample type, particle distribution can be determined only in layers sufficiently thin to allow the emitted radiation to pass through the layer without being fully absorbed. Since most radioactive particles emit various types of radiation, the layer thickness must be selected according to the detector type, i.e. the thinnest layers should be used in case of alpha detectors (a thickness less than 100 μm is desirable), while thicker layers can be applied in case of beta and gamma detectors. Most mass spectrometric techniques require that particles be fully dissolved prior to measurement.

Monitoring techniques

Standard monitoring/screening techniques for the detection of elevated levels of activity are adequate for localization of radioactive particles in the field or in environmental samples. These techniques provide information about hot spots and are not directly applicable for the identification of single radioactive particles.

Typically, portable devices with gas ionization detectors, scintillation crystals or semiconductor detectors (usually GM counters, NaI(Tl) scintillators and HPGe detectors, respectively) are used in field measurements. While thin window GM counters are sensitive to beta particles, NaI(Tl) and Ge detectors are more appropriate for the detection of gamma radiation. Surface contamination monitors and α-β counters are applicable for checking solid surfaces. Obviously, gaseous or liquid materials cannot be controlled as bulk samples, but thin layers are easily produced by filtration.

Beta detectors have been used for monitoring samples by Rao [26], Falk [27], Mandyukov [28], and Vapirev [29, 30], while gamma spectrometry with NaI(Tl) or HPGe detectors was applied by Lokan [6], Salbu [11, 12, 13], Balashashy [31], Pöllanen [32] and Romero [33].

Sampling techniques

Standard sampling techniques for soils and sediments [34] include soil coring and grab sampling. Soil and sediment samples should be dried at room temperature only, as surface structures can be corrupted at high temperatures. Dried, ground and milled samples are spread for surface monitoring purposes. Similar to grain size analysis, solid samples can be divided into different coarse fractions by sieving the sample through a set of sieves. The fine fraction, below 100 μm, can be further differentiated into the μm size range using a microparticle classifier.

The Bahco apparatus is a combination of air centrifuge-elutriator where particles dispersed in a spiral air current are scattered into two streams dependent on aerodynamic parameters; by varying the flow, a series of size fractions can be obtained. Measurements made by Burns [35] on the former weapons test site on Maralinga and Emu showed that the mass distribution of the soil among the different particle size fractions varied significantly from the activity distribution of the same fractions. At the given area, soils were characterized as sandy with the greatest mass generally associated with the 250–500 μm fraction, while a considerably higher proportion of Am and Pu were found in the finer (inhalable) fraction.

It was confirmed by several authors that – except in areas which were disturbed through ploughing – most of the activity remained in the top layer of the soil. Therefore, surface monitoring techniques can be effective for radioactive particle identification many years after the occurrence of the contamination. On Maralinga and Emu, Burns [36] found that the activity remained in the top 1 cm soil layer more than 30 years after the explosions. Fifteen years after the Chernobyl accident, similar results were published by many scientists performing soil profile measurements both in the vicinity of the Chernobyl NPP and in far distances. Depth distribution also depends on soil type and on the nuclide in question. To make the localization of radioactive particles in soil and sediment samples easier, information on particle size distribution associated with different emission sources and different soil types as well as the expected depth distribution would be most useful.

An alternative approach to the determination of particle size distribution is to perform resuspension studies as was utilized at the former British test site in Australia [35]. Using this technique, the characteristics of the inhalable dust can be determined. Dust-laden air was generated in a reproducible way in a dust-raising apparatus, and the inhalable component was classified using a cascade impactor. The AMAD value (activity median aerodynamic diameter) was about 6 μm and referred to as inhalable fraction (0–11 μm) at the studied areas.

There are standard techniques to sample aqueous systems [34]. Filters of different materials and pore sizes can be applied simultaneously. Radionuclides associated with particulate or colloidal matter can be separated by filtration and ultrafiltration, and the size fractionation can be determined by means of a set of membranes with cut-off values into the submicron sizes. Colloidal material (<0.45 μm) can be separated using hollow fibre ultrafiltration and tangential flow systems [12, 13].

With a peristaltic pump, water is sampled and transferred into a molecular mass discriminator where ultrafiltrates are obtained. For volumes in the range 1–100 L, hollow fibre ultrafiltration can be utilized, while tangential cross/flow cassettes can be applied for larger volumes. When hollow fibre filtration is on-line interfaced with ion exchange chromatography, radionuclides associated with charged and neutral colloidal species can be differentiated simultaneously [12, 13, 18, 20].

In contrast to bulk samples, radioactive particles retained on filter membranes are relatively easy to identify. Unfortunately, there are few published articles on radioactive particles in aqueous systems, especially about colloids which do not settle under the force of gravity. Results obtained by Salbu et al. [20, 37] on effluents from Sellafield demonstrated that a major fraction of radionuclides including transuranium elements was associated with particles and a minor fraction was present as colloids. Similar results have been reported about the distribution of radionuclides among different size fractions in the effluents from the nuclear installation at La Hague, France. Hamilton et al. [38] studied alpha emitters in the Irish Sea and found significant amounts in the air-water interface layer as well as in the sediments. He distinguished artificial alpha emitters from those of natural origin and showed that the latter ones could be attributed to the presence of radioactive particles.

Aerosols were frequently studied after nuclear weapons tests and also after the Chernobyl accident. Standard environmental monitoring stations are usually equipped with aerosol filters of different capacity, using different types of filter material [34]. Some of them operate batch-wise, while others work continuously with a moving filter band. In addition to the standard filtration techniques, there are systems separating the aerosols into different size fractions. Size-selective inlets are used to define the particle size fraction being sampled. Air is drawn through these inlets to remove particles which exceed a specified aerodynamic diameter. Several inlets are placed in a series, in the form of a so called ‘cascade impactor’ to obtain more detailed size distribution of the aerosols. By this technique, several fractions of different aerodynamic diameters are obtained that can be further investigated.

Sample splitting

In binary separations, samples are separated into two parts of nearly equal mass, each part is counted and the specific count rates are determined. The procedure of splitting and counting is repeated until the desired small fraction size containing the radioactive particle is reached. Besides sample dividing into halves as in binary separations, samples can be split into more than two sub-samples of comparatively equal masses.

Statistical evaluation for detecting radioactive particles in environmental samples by sample splitting was performed by Bunzl [39]. The probabilities for detecting radioactive particles in this way were calculated using the Monte Carlo method as a function of the number of radioactive particles in the original sample, the number of sub-samples used, the frequency distribution of the activities of the radioactive particles and the precision with which the activities of the sub-samples were determined. He concluded that the presence of radioactive particles in the environment could be detected with fairly high probability by sample splitting.

The wider the frequency distribution of the radioactive particles’ activities, the smaller the number of sub-samples necessary to detect the presence of radioactive particles within a given probability. Unless there is a strong indication of the presence of a large number of particles in the sample (>5), the particles will usually be detected with a probability >95% by assessing 3–4 sub-samples. Bunzl also concluded that it is not effective to increase the precision of the activity measurements of the sub-samples at the expense of the number of sub-samples investigated.

Burns used the process of binary separations for soil samples from test ranges at Maralinga and Emu [35]. The original sample of 800 g with a total activity of about 25 Bq (^{241}Am) contained 54 radioactive particles which accounted for almost all of the activity in the sample.

Sample splitting has been used for RP isolation in combination with autoradiography [11, 40], beta counting [27] and gamma spectrometric detection [32, 33] by several authors. In some cases sample splitting was replaced by cutting high activity spots from thin sample layers, most probably from filters as was done for aerosols by Saari [41] and Güter [42], and for sediment layers by Hamilton [38]. Saari used autoradiography to determine particle distribution while the latter authors applied nuclear track detectors for the same purposes.

Several authors, such as van der Veen [43], Pollanen [32], Falk [27], Saari [41], Mandyukov [28], Vapirev [29, 30] and Salbu [11, 12, 13], used adhesive tapes for particle isolation in samples such as cloth, sediment, soil, plant leaves and other outdoor surfaces.

Fractionation techniques applicable for radioactive colloids and particles in the environment are outlined in more detail by Salbu [13].

3.1.2. Particle location and re-location

The specialized sampling techniques of environmental particles (sieving and spreading solid samples, collecting particles on swipes, filtering gases and liquids) are aimed at producing a thin layer of particles, evenly dispersed and well separated, over a substrate (e.g. graphite or silicon planchettes, membranes). Suspension of particles from a cotton swab by ultrasonication in an organic liquid followed by spreading and drying over graphite planchettes is commonly used in many laboratories. Nonetheless, the particles-of-interest (POIs) are almost invariably mixed with a large population of non-POIs. Particle location techniques have to be applied to find and identify the POIs.

‘Passive’ and ‘active’ methods can be utilized in order to identify those particles-of-interest (among all others) that are potential candidates for further analyses. The ‘passive’ methods (section 3.2) include alpha-, beta- and gamma spectrometry, real time imaging techniques, and alpha- and gamma-autoradiography. The ‘active’ methods, based on the detection of stimulated radiation emitted by the POIs while being irradiated by neutrons, ion-, photon- or electron-beams, include fission-track-analysis (FTA), electron microscopy and microanalysis, and mass spectrometry techniques such as SIMS, LA-ICPMS or AMS (see sections 3.2 and 3.3).

The particle search is carried out in the source instrument, yielding a list of POIs and their coordinates in the coordinate system. To identify the POIs, 2, 3 or 6 readily discernible reference point marks are introduced into the sample plane and also identified by their coordinates. Then, the sample is transferred to a target instrument where the POIs are repeatedly relocated by applying a coordinate transformation method, i.e. a 2 point, 3 point (the triangulation method) or 6 point relocation algorithm. A detailed discussion of the methods as well as the estimated uncertainty of the relocation method has been given by Admon [44]. By repeatedly applying the location and relocation methods, the same identified particle can be analyzed by a variety of non-destructive microanalytical techniques, often in remote laboratories, prior to its isolation and destructive handling.

3.1.3. **Particle isolation, micromanipulation**

Large particles having certain colours can be extracted under microscope. However, physical extraction represents a challenge for small particles. In some cases, splitting and counting techniques can reduce the number of soil and sediment particles significantly, but not completely. In other cases, the isolation technique seems to be only applicable for extremely ‘hot’ particles that could be fixed on adhesive tapes using a simple surface monitor without special preparations, as demonstrated for the removal of radioactive particles from the trousers of a traveller returned from Kiev right after the Chernobyl accident [45].

When beam based methods are used (e.g. SEM, TEM, SIMS), single particles can be characterized without physical extraction. New methods have recently been developed for the manipulation of single particles in the size range down to 1 μm and above under a light microscope and for particles smaller than 1 μm directly under the scanning electron microscope [44].

Micromanipulation under a light microscope

Simple manipulations of single particles, such as lifting and depositing, can be performed by a micromanipulation system comprised of a light microscope, a precision x-y-z specimen stage driven by micrometres, and an x-y-z micromanipulator capable of holding different needles. A CCD camera and a precision stage are desirable options. Both binocular and stereo microscopes are adequate for viewing and processing the particles.

Two types of needles serve in the micromanipulator: metallic (e.g. steel, tungsten), and non-metallic (such as graphite, glass, tungsten-carbide, and plastic). In some cases glue is applied to the needle tip to lift off particles. Electrostatic charging effects have to be considered during manipulations. They can be eliminated by coating needles with a conductive layer (gold, platinum). A rotary horizontal needle holder has been constructed [44] that allows the axial rotation through 360° of the particle at the tip of the needle for performing μ-tomography and μ-diffraction studies at a synchrotron.

Micromanipulation systems based on binocular light microscopes and stereo light microscopes were built and operated at the IAEA Laboratories, Seibersdorf by Admon [44]. Depleted uranium particles were located and identified in soil samples by μ-XRF scans. Selected particles could then be successfully re-located under the stereo light microscope by applying the 3 point algorithm, lifted by graphite needle and brought to the synchrotron for μ-XRF tomography (‘virtual slicing’) and to a FIB for micro-surgery (‘real slicing’).

Micromanipulation in-situ using a scanning electron microscope

Micromanipulation of individual particles in situ using a scanning electron microscope (SEM) has been reported. SEM serves as the source instrument where POIs are identified based on their morphology or elemental composition. Then the internal micromanipulator installed in the SEM can be operated directly on the sample. Selected POIs were separated, lifted and transferred to target planchettes for SIMS and ICP-MS investigations by Sakurai and Esaka [46, 47]. It has been shown that in-situ micromanipulation allows separation between adjacent micron-sized particles [47]. Micromanipulation of airborne sub-micron pollutant particles has also been reported [48] using in situ SEM.

Micromanipulation using atomization techniques (laser ablation/desorption or ion beam sputtering)

Laser light and sputtered ion beams can be used to remove radioactive particles from thin sample layers or certain parts of single particles. More details on these techniques are given in Section 3.4.

Micro-surgery of radioactive particles

The inner microstructure of a particle can be revealed either by virtual slicing, which is performed by µ-tomography using the intensive X ray source of the synchrotrons (see Section 5), or by real slicing by means of an energetic focused ion beam (FIB) in the recently developed FIB dual-beam instruments. A particle fixed to the needle of the micromanipulator can be imaged and microanalyzed, while the FIB using Ga+ ions makes ultra-thin slices of the particle.

It was reported that a 200 µm DU-oxide particle, a corrosion product of a DU ammunition fragment collected in Kuwait, was sliced by the sub-micron focused ion-beam while viewed in a dual-beam FIB. With the use of a second micromanipulator-driven needle, the removed ‘slice’ was fixed and further studied. Inter-granular pores and titanium inclusions were detected (U. Admon, Pers. Comm.).

The FIB slicing technique is direct and fast, providing information about the inner structure of the material. It has proven to be a useful tool in transmission electron microscopic (TEM) sample preparation in material sciences, but has not yet been used for radioactive particles.

With the recent improvements in micromanipulation, multiple analyses of one individual radioactive particle can be made through the use of different micro- and analytical techniques for the characterization of different properties.

3.2. NUCLEAR ANALYTICAL TECHNIQUES TO STUDY RADIOACTIVE PARTICLES

A great variety of nuclear measurement methods have been applied to radioactive particle studies since the first release of anthropogenic radionuclides into the environment. Gamma, beta and alpha measurements have been used not only to identify radioactive particles, but also to determine the isotope composition of radionuclides, previously in bulk materials and presently in radioactive particles. Nuclear measurement methods went through significant improvements during the last half century. Using current knowledge, one can see that very good results were obtained with quite simple techniques and that many theoretical questions about the distribution, fractionation and migration of radioactive materials were evaluated in the early 1950s and 1960s.

3.2.1. Gamma spectrometry

Gamma spectrometry has always been the basic technique for investigating radioactive particles. At the beginning, NaI scintillation detectors did not provide high resolution, but in many cases the major components of the fallout from explosion tests could be determined. Fission products such as I, Cs, Zr, Nb, Ce, Mo, Tc, Ru, Ba, and La radioisotopes could be identified based on the scintillation spectra as well. To obtain better selectivity and higher accuracy, radiochemical separations were often performed. At the University of Arkansas, Ba-Sr, Mo-Te-Sb-Sn, Zr-Y-lanthanoids, Cs, and Ru-I fractions were chemically separated and then further purified. Uranium and Np were also chemically processed [49]. BGO detectors of high counting efficiency have also been used successfully for identification of radioactive particles in environmental samples [32, 50].

When high resolution gamma spectrometers, initially with Ge(Li) and later with HPGe detectors, appeared, they step by step replaced scintillation detectors in gamma spectrometric measurements. Mamuro et al. [51] used both types of detectors already in 1969. High-resolution gamma spectrometry became a standard technique in surveys revealing the environmental consequences of the Chernobyl accident after 1986.

With the development of portable gamma spectrometers, high resolution gamma spectrometry was introduced in field studies. Methods were developed to calculate activity concentrations from the measured field data taking into account specific geometry and self-absorption [52]. Today, in situ gamma spectrometry is routinely performed and a great number of articles have been published on the application of this technique.

Using up-to-date nuclear measuring methods, retrospective analyses of contaminated areas have been performed and environmental surveys have been initiated at several former nuclear weapons test sites. Residual radioactivity measurements were started at Maralinga and Emu in the 1980s, and environmental survey programs were performed in Kazakhstan, in the Mururoa and Fangataufa Atoll, and on the Marshall Islands during the 1990s [5–8]. Under water gamma detectors were also applied in the Joint Norwegian-Russian expeditions (1993–1994) to the Kara Sea [23].

In the vicinity of the firing pads gamma spectrometry was very often used to detect americium as well as Pu isotopes [5, 6, 7, 35, 36]. Many years after the explosions, the amount of ^{241}Am, due to the decay of its parent ^{241}Pu, has increased and in many cases exceeded the detection limit for gamma spectrometry. Thus, gamma spectrometry became useful for the direct detection of ^{241}Am, an indicator of transuranium contamination that is typically present in the form of particles.

3.2.2. Beta counting

The beta counting technique has a widespread application for detection of anomalously high activities, typically using GM counters. In the case of relatively high contamination, it can be used as a surface monitor to detect hot spots, because many of the fission products emit beta radiation. The method is not selective.

Beta spectrometry is typically used for the identification of beta emitters after a tedious, time-consuming radiochemical separation procedure necessary because the beta spectra from different nuclides often interfere. ^{90}Sr, ^{89}Sr and other pure beta emitters are usually determined by this method, e.g. [53].

Based on small sized radioactive particles, self-absorption of high energy beta particles is of minor importance. It is possible to detect some beta emitters with high maximum beta energy directly from the beta spectra without chemical processing, but this requires a proper self-absorption. Using these principles, 'Barium' radioactive particles were analyzed for strontium isotopes and ^{144}Pr by Vapirev [29]. So-called 'non-destructive beta spectrometric analyses' have been performed by Mandjoukov [28]. The application of this technique is significantly affected or limited by the composition of radionuclides in the investigated sample.

Many years after the Chernobyl accident, the major contributor to the high energy beta radiation of the samples is ^{90}Y, the daughter of ^{90}Sr. The activity of ^{90}Sr in environmental samples can be roughly estimated without radiochemical processing by the direct detection of high energy beta particles emitted by ^{90}Y.

Using liquid scintillation counters, beta spectrometry can be carried out at nearly 100% efficiency for many radionuclides, as demonstrated in the literature [5, 32, 54].

3.2.3. Alpha spectrometry

Alpha spectrometry is a sensitive nuclear analytical technique for the determination of alpha emitting nuclides e.g. transuranium isotopes. Because of the extremely low penetrating power of alpha particles, it can be applied to thin samples only, preferentially infinitely thin sources that are prepared from environmental samples by radiochemical procedures. Most of the methods are based on radiochemical separations followed by alpha spectrometry using Si semiconductor detectors. Alpha spectra can also be obtained with gas ionization and liquid scintillation counters.

So-called gross alpha measurements without chemical treatment have been applied [30, 31]. However, these measurements have limited use, unless only one alpha emitter is present in the sample. For surface monitoring purposes they are not reliable because of self-absorption.

If radioactive particles are isolated from the bulk material, alpha spectra can be obtained by direct measurement. The alpha spectra thus obtained are still deteriorated; and the energy resolution is often significantly reduced by the self-absorption taking place within the particle. Pöllanen [55] developed the AASI-SIKA software package that can unfold alpha spectra of poor resolution, if the size and shape parameters of the radioactive particle are known. The performance of the code was demonstrated by evaluating the alpha spectrum of a radioactive particle originating from the Thule accident. Using this alpha spectrometric measurement, the radioactive particles remain intact for further analyses.

The spatial distribution of radioactive particles and radioactive particle concentrations can be determined in the simplest way by autoradiography and solid-state nuclear track detectors (SSNTD).

3.2.4. Autoradiography

In autoradiography a photographic film sensitive to beta (or sometimes to alpha) particles is exposed to radiation and then developed using standard photographic techniques. Blackening in autoradiograph spots corresponds to the particle activity. The calibration procedure for debris from nuclear weapons tests was discussed by Sisefsky [56]. Activities roughly proportional to volume were found in fallout particles.

Autoradiography is the oldest technique that has been used for the determination of activity distribution of environmental samples including those originating from weapons tests [26, 40]. It was also used to study samples contaminated by fallout from the Chernobyl accident [11, 41, 43, 57, 58] and is still in use owing to the easy and simple way of its performance [59]. The introduction of electronic autoradiography using phosphorus image systems has improved the technique significantly, as shown in Section 3.2.6.

3.2.5. Nuclear track detection

Alpha particle detection

In solid state nuclear track detection (SSNTD), plastic foils are brought into close contact with alpha emitting radionuclides. As a result of the interaction of alpha particles with the plastic, chemically etched tracks are formed. The tracks are measured under a microscope or automatically evaluated by a track analysis system. Solid state nuclear track detection has been used for alpha particle measurement from the 1980s onwards. Nuclear track detectors have been widely applied in the analysis of environmental samples [4, 38, 43, 58, 60, 61]. Solid state nuclear track detection is superior to autoradiography as it provides information not only about the spatial distribution, but also about the alpha emitting nuclide composition of the radioactive particles.

Track parameters, i.e. the minor axes and the track diameter, allow reliable separation of tracks according to alpha particle energy. Alpha spectrometry with SSNTD of environmental samples contaminated by the Chernobyl accident has been performed by several authors [60–65]. Although its resolution is much less superior to that of alpha spectrometry, SSNTD has the advantage of simplicity. Thus a great number of samples can be treated and evaluated.

Recently a new evaluation method has been developed for the measurement of the size and the activity of alpha emitting radioactive particles that produce characteristic radial clusters of tracks in etched films [62]. An automated image analyzer calculates the actual track parameters (track co-ordinates, azimuth angle, dip angle, track range), projects the track paths above the plastic surface, and determines the major parameters of the radioactive particle (i.e. alpha activity, physical size and distance from the plastic surface).

Fission track detection

In fission track detection, the sample in close contact with the nuclear track detector is irradiated by neutrons and the tracks initiated by the high energy fission products are analyzed. Thus, nuclear track detectors can be used both for detection and differentiation between alpha emitting and fissile nuclides.

Fission track analysis (FTA) is a fast and efficient method for searching fissile material in radioactive particles. In combined FTA-SEM analysis, FTA is used for localizing particles that are subjected to further studies by SEM.

Boulyga [66] used NTDs to detect both alpha particle and fissile material as neutrons and gamma radiation initiate (n,f) and (γ,f) reactions, respectively. The size of radioactive particles, the activity and the U content have been determined in aerosol samples by NTD technique. Alpha and fission track detectors were used by Vlasova [67] to identify actinide bearing micro-particles in the sediment of the Yenisey River. Böhnke [68] applied film autoradiography and alpha NTD to detect radioactive particles of natural origin in environmental samples.

3.2.6. Real time imaging techniques

Real-time digital imaging systems (RTDI) provide an image of the radioactive particles during a relatively short time compared to autoradiography and nuclear track detectors. Thus, they can replace the conventional techniques for identification of radioactive particles.

The advantages of the real-time imaging systems compared to conventional autoradiography are the following:

- The RTDI techniques are faster.
- It is easy to determine the position of the particle.
- The results are displayed in real time; there is no need for processing the image after exposure.

Two types of digital image systems have been used to detect radioactive particles in sediment samples by Eriksson [69]: the scintillator beta based camera and the silicon based bioscope. Both techniques have got a widespread application in nuclear medicine.

The detector of the beta camera is a scintillator of about 0.3 mm thickness that emits light in the de-excitation process. The light travels through a fibre optic face plate to a photocathode, where photoelectrons are emitted and are accelerated in multichannel plates. The resulting cascades of electrons produce a detectable signal at the anode. The position of the event and the electric signal proportional to the energy of the incident ionizing particle are determined in the camera. The beta camera used by Eriksson was produced at the Department of Radiation Physics at Lund University and had a spatial resolution of 0.5 mm with a detector diameter of 40 mm.

The detector of the IDE bioscope is a 0.3 mm thick double sided silicon strip sensor. The strips are located on both the p and n sides and have a width of 50 µm. The strips of one side are placed perpendicular to the strips on the other side. The energy deposited by an ionizing particle in the detector is proportional to the kinetic energy of the particle, allowing the measurement of the activity distribution. The signal is processed by a self-triggered read-out data chip. The bioscope used by Eriksson [69] was manufactured by the Integrated Detector & Electronics AS and had a sensitive area of 32×32 mm^2 and a system resolution higher than 50 µm.

The beta camera had a higher sensitivity than the IDE bioscope. Although the IDE bioscope had a better spatial resolution, it required a counting time 4 times longer than for the camera to collect the same number of counts from the same particle. The beta camera has been used by Eriksson [69] to identify radioactive particles in sediment samples originating from the Thule area (Greenland) and contaminated by U/Pu particles.

Zeissler [70] reported the use of digital autoradiography by phosphor and semiconductor array systems. The semiconductor pixel array detector is basically a bioscope, with a phosphor plate based on a BaFBr:Eu scintillator, (made by Fuji Instruments), and 20 × 25 cm plates, with 25 µm resolution. A photomultiplier is used to detect luminescence emitted from the phosphor upon stimulation by a He-Ne laser (photo-stimulated luminescence). The intensity of the luminescence is proportional to the emission rates of radioactivity previously recorded by the phosphor. Phosphor image systems have been used for the localization of radioactive particles from a series of contaminated sites.

3.2.7. Other methods

Several other nuclear measuring methods that have been developed for the detection of ionizing radiation are tentatively applicable for the measurement of radioactive particles after preliminary isolation of the particle, supposing that the detection limit is sufficiently low for the detection of single particles.

Recently special methods have been developed for the determination of doses from radioactive particles, taking into account the absorption within the particles. Corresponding doses can be calculated by different methods. Monte Carlo simulations are used to calculate self-absorption corrected doses [71]. The VARSKIN code, originally used to calculate skin doses due to distributed contamination, has been modified to calculate 3-dimensional doses from radioactive particle calculations corrected for self- absorption [72].

There are different methods for the direct measurement of radiation emitted from particles. Besides TLD, exoelectron dosimeters and radiochromic dye foils have also been developed. In exoelectron dosimeters [73], upon exposure to ionizing radiation, electrons near the surfaces of certain crystals become excited to higher energy states and a fraction is held in impurity traps. Upon heating, these low energy exoelectrons are emitted and detected using windowless gas flow counters. The emission can be considered a surface phenomenon, ideal situation for measuring beta doses.

Radiochromic dye foils require no processing: they change colour upon irradiation and are evaluated with appropriate densitometers. By this method, 3-dimensional dose maps can be directly obtained [74]. Exoelectron dosimeters and radiochromic dyes were calibrated and tested using standard extrapolation chambers [72, 75, 76].

3.3. MICROANALYTICAL TECHNIQUES TO STUDY RADIOACTIVE PARTICLES

Microanalytical techniques deal with the analysis of (sub)millimetre ranges of materials such as single particles. Results are difficult to obtain because very sensitive techniques are required to detect the small masses and usually high spatial resolution is needed to determine lateral distribution. To obtain information about the elemental composition of particles and about the physico-chemical structure, spectrometric methods similar to those used for bulk analyses are applied. To determine spatial distribution, samples are excited by various beams of (sub)millimetre sizes.

3.3.1. Production of spectra

To meet special demands, different beam techniques have been developed. In the various analytical methods, electrons, heavy elementary particles or photons are used to excite the atoms causing nuclear reactions or extranuclear electronic transitions. Photons are also used to affect atomic and molecular movements. As a result of the different ways of excitation, quantized energy transitions take place followed by quantized de-excitation processes when radiations of discrete energy are emitted. Spectra obtained by detecting the energy distribution of the radiations reveal the elemental composition or the chemical bindings/structure of the sample.

Electrons, protons, charged particles and photons (including X rays, visible light photons, heat) can excite extranuclear electronic transitions, producing characteristic X rays and light photons that carry information about the elements emitting the radiations used in X ray fluorescence (XRF), optical (ultraviolet and visible light) emission spectroscopy (OES) as well as flame photometry.

Atomic absorption spectroscopy (AAS) measures optical absorption and reveals elemental composition by measuring absorption of characteristic lines one by one. Infrared light photons can excite vibrational and rotational energy levels, and the measured absorption (IR spectroscopy) characterizes the chemical bonds. Nuclear reactions are also produced by elementary particles, usually by neutrons, but protons, charged particles or in some cases gamma photons can also induce nuclear transformations. Neutron activation analysis (NAA) is based on the gamma spectrometric detection of either the prompt gamma or the delayed gamma radiation emitted by the radionuclides produced in the nuclear reaction.

Besides the analyses of absorbed or emitted radiations, very often scattered (elastically) and transmitted radiations are also determined, providing information about the morphology and crystal structure of the sample, e.g. in microscopic diffraction and tomographic measurements. In case of microprobe studies, the various interactions of the primary beam with the matter are simultaneously recorded, thus obtaining information about the elemental composition and the structure of the sample simultaneously.

A very good review of recent advances in microanalytical techniques done by Jambers et al. [77], provides examples for the analysis of individual, non-radioactive environmental particles including aerosols, sediments etc.. An excellent summary about microscopic X ray fluorescence analysis was published in 2000, edited by Janssens, Adams and Rindby [78]. Microanalytical techniques have been applied for the characterization of radioactive particles only in a few cases. The principles of the techniques and examples of RP analysis are given in Sections 3.3.2 to 3.3.6.

3.3.2. Microscopic beam techniques – generalities

The elemental composition of microscopic particles is often determined by X ray emission techniques i.e. by μ-X ray fluorescence (μ-XRF), μ-particle-induced X ray emission (μ-PIXE) and electron probe microanalysis (EPMA). These three methods only differ in the type of energy carriers that are being used in the primary beam to eject core-level electrons from the target atoms. In each case the resulting characteristic X rays are detected to identify the elemental composition.

Interaction volume

The exciting beams consist of X rays, protons (or other charged particles) or electrons that have different penetrative power. Depending on the type of particles or radiation, their energy and the composition of the sample, i.e. density and atomic number, the penetration depths vary significantly. Furthermore, beam size differs according to the type of radiation and the techniques used for beam focusing. Thus, excitation takes place in interaction volumes of different sizes to provide information on the local composition.

Comparing the penetrative depth of 20 keV X rays, 20 keV electrons and 2.5 MeV protons in light matrices (atomic number <20, density <2.5 g/cm^3), the penetration ranges are 1000–10000, 4–6 and 50–70 μm, respectively. Typical beam sizes are 5–10 μm for capillary X rays or 2nd generation synchrotron X rays, and 3rd generation synchrotrons microbeams of 0.7–2 μm can be produced. Electron beams (of 1 nA) can be focussed down to 10 nm, but the beams – as a result of energy losses via collisions of the projectiles – broaden into pear-shaped interaction volumes of 1–5 μm. For protons, the typical beam sizes are 1–5 μm.

Detection limits

The detection limit for a given element is basically determined by the photo peak intensity and the corresponding background intensity. Thus, sensitivity can be increased by increasing the elemental X ray yield, the beam intensity or the data collection time, or by decreasing the background.

X ray yields are determined by the X ray emission cross-sections that are comparable for all three projectile types (X rays, electrons, protons). For protons and electrons (charged particles), the cross-sections decrease with increasing atomic number, thus sensitivities in PIXE and EPMA are higher for light elements, while the photo-ionisation process favours heavier elements. These tendencies are valid for thin samples. As the sample thickness increases, X ray photons, due to their larger penetration power, will excite more atoms. For massive samples, the sensitivity for XRF will increase, while EPMA will remain the least sensitive technique.

In case of XRF, the background originates mainly from scattered photons on the low energy side of the primary exciting energy, while charged particle interaction results in a bremsstrahlung continuum. This continuum is especially noticeable in EPMA and is suppressed in case of PIXE, because it is caused by low energy secondary electron.

When microscopic particles are analyzed, not only the nature of the projectiles but also the size of the beam relative to that of the sample becomes important. For particles smaller than the beam, only a part of the total flux is employed and the unused part of the beam may contribute to the background. Thus, beam size may also influence the sensitivity and be a limiting factor, especially for XRF techniques based on poor beam focusing.

3.3.3. Electron beam techniques

In electron beam techniques, a nanometre-sized electron probe generates various signals on sample interaction. Backscattered and secondary electrons or transmitted electrons can be detected in addition to emitted X rays. Based on the detection of backscattered and secondary electrons, morphological information can be acquired in scanning electron microscopy (SEM), while compositional information is obtained by the wavelength- or energy-dispersive detection of emitted characteristic X rays in SEM-WDX and SEM-EDX, respectively. Scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) use transmitted and diffracted electrons.

In electron probe microanalysis (EPMA), the same type of measurements is performed. Originally SEM was mainly used to obtain high resolution images and the chemical analysis was performed by EPMA. The differences have been significantly reduced over the years and now both chemical and morphological studies are nearly equally possible by both techniques, the choice of technique resting on practical arrangements.

Scanning electron microscopy techniques

Due to the small size of the electron beam used in the SEM (down to a few nanometers) and to the size of the beam-specimen interaction volume, SEM images have the best spatial resolution at the (sub)micrometer range. Elemental detection limits by EDX are typically 0.1% (0.01% in WDX), and the detectability of light elements is to some extent limited. However, recent developments include improved electron optics, faster EDX detectors and more efficient image processing systems, allowing the acquisition of better electron images and higher quality elemental analyses and maps. Ultra-thin-window EDX detectors offer possibilities of detecting light elements such as B, C, N, and O. EPMA and SEM-EDX have been successfully used for the analysis of single particles, aerosols, suspensions and sediments (both radioactive and stable) [77].

Transmission electron microscopic techniques

In transmission electron microscopy (TEM), thin samples are illuminated with electrons and the transmitted electrons are detected. When the whole imaged area is illuminated simultaneously, the magnified image can be displayed on a fluorescent screen. In scanning mode of operation (STEM), the specimen is scanned with a small electron probe focused to a diameter of a few nm or less and the transmitted electrons are recorded with electron detectors, computer processed and displayed on a monitor.

The transmitted electrons can be recorded in bright- and dark-field modes and provide morphological information. Scattered electrons can be detected as back-scattered (BSE) and secondary electrons (SE). BSE are used to identify crystalline specimens by their crystalline structure in electron diffraction.

X ray microanalyses of small areas of thin specimens are possible by attaching an energy-dispersive X ray analyser (EDX) to STEM. STEM of thin samples combined with EDX provides the best lateral resolution both in imaging and X ray fluorescence analysis. However, STEM-EDX can only perform limited analysis of single particles or environmental samples, because the preparation of thin samples is a crucial point in the technique.

STEM-EDX can be combined with electron diffraction to study crystalline phases. Using electron diffraction (SAED) in selected sample areas, the crystallographic structure of the sample spot of micrometre size can be studied. Colloidal radioactive material in the Sellafield and La Hague effluents was analyzed by transmission electron microscopy (TEM) by Salbu et al. [20, 37]. Colloidal material with particle sizes of about 20 nm and pseudo-colloids in the region of 100 nm were identified.

Electron energy loss spectrometry

In electron energy loss spectrometry (EELS) instruments, a magnetic prism spectrometer is integrated in the optical column of a conventional TEM and the final image is registered as an energy-selective (filtered) image. By scanning the sample over a small slit, the energy loss spectrum is sequentially recorded and analyzed using a personal computer as a multichannel analyser. The energy-filtered images can be transferred to an image processing system, thus element specific images are obtained. The main advantages of this technique are the high sensitivities for elements of low atomic number and the information about the chemical bindings and the electronic states included also in the spectra (electrons produced in primary interactions with matter give rise to signals). The major drawbacks of the method are the following:

- It can only be applied to very thin samples that allow the transmission of electrons;
- Because of the long illumination and recording time, mass losses, especially in case of volatile components, can occur.

In parallel spectrum recording systems, the collection time is reduced significantly, also minimizing material losses. Parallel EELS can be used to analyze fine particles of environmental samples, and for example the carbon content can be mapped. However, no applications related to radioactive particles have been reported.

Examples of analysis of radioactive particles by electron beam techniques

The most frequently used microanalytical technique in radioactive particle studies is electron microscopy, typically scanning electron microscope combined with X ray emission analysis. This powerful technique could not be applied for the study of particles due to worldwide fallout from nuclear testing in the 1950s and 1960s as it had not yet been developed; thus retrospective investigations are very valuable. In 1985, Grüter [43] analyzed a giant radioactive particle of 64 μm that had been collected in 1962 in Germany and that had probably originated from a Russian test explosion carried out at the Novoya Zemlya test site. According to SEM-EDX measurements, the dark porous particle contained a significant amount of U besides the elements typical for soils and aerosols.

Salbu et al. [11, 12, 13] compared the properties of radioactive particles collected within the Chernobyl accident 30 km zone in 1987 with those of particles collected in the vicinity of the Windscale Nuclear Installation in 1956. According to SEM-EDX measurements, particles from the Chernobyl accident had a compact crystalline structure with a relatively uniform surface U layer. Particles of small (1–2 μm) spherical U granulates were also identified, and several particles had a Pb cover. Particles released from Windscale had a flake-like layered structure, varying in size (10–250 μm), with a U cover.

Radioactive particles of Chernobyl accident origin collected in different parts of Europe were frequently studied by SEM-EDX/EPMA. They were discovered, identified and analyzed by Devell et al. [79] in Sweden, and spherical particles up to 1 μm size were identified by SEM. Falk [27] found two groups of particles, fuel-like particles and Ru/Rh ones. The elementary composition of the first ones was dominated by U, while the second ones contained Ru and Mo metals as well as Tc, Fe and Ni. Particles of similar composition and morphology were found in Finland. Raunemaa et al. [80] analyzed particles of 2–10 μm size by SEM and EPMA. Fuel-like particles consisting of U and some Zr and Ru particles were identified. Saari et al. [41] also analyzed particles originating from the Chernobyl accident and collected in Finland. The main bulk composition of the particles was found to be U. The average aerodynamic size was 10 μm, and the particles were rectangular or pentagonal in shape. Pöllanen et al. [32] performed a detailed analysis of a single particle separated from marine sediment including SEM and EDX measurements, proving the Chernobyl origin of the particle. Schubert et al. [81] studied nuclear fuel and metallic precipitate type particles collected in Poland by SEM and EPMA. One fuel-like radioactive particle was found to be high in U content together with O. In contrast, metallic precipitate type particles high in Ru also contained Fe, Ni, Mo, Tc, Rh and Pd, but no O was found.

Vapirev performed electron microprobe studies on ‘Ba’ and ‘UO_2’ type radioactive particles found in Bulgaria [31]. The former ones proved to be Ba-Sr-Zr particles according to EPMA [29]. These particles were either monolithic or porous with mean size of 8.5 μm, and contained Zr and Pb as well as U [28].

3.3.4. Particle beam techniques

In proton or particle beam techniques, a collimated ion beam a few micrometres in size bombards the sample surface and interacts with matter. Most frequently 1–3 MeV protons are utilized. The high energy proton beam is obtained by means of cyclotron or Van der Graaff generator and focussed with magnetic quadrupoles and/or electrostatic lenses. The proton beam current is usually limited to 100 pA to avoid damage to the sample, although some losses of volatile compounds e.g. organic materials can occur due to the necessary vacuum in the sample compartment.

Particle induced X ray emissions

In particle induced X ray emissions (PIXE), charged particles ionize the inner shells of atoms and characteristic X rays are detected. The energy-dispersive detection system measures the X ray spectrum at each beam position, while the beam is scanned over the sample. The acquired elemental maps composed by a computer are very similar to EPMA maps, but have better detection limits (1–100 ppm) and inferior spatial resolution (0.5–10 μm). Elemental images can be displayed simultaneously and saved X ray spectra can be recalled for the purposes of detailed quantitative analysis.

PIXE was used to provide elemental concentrations and maps of the distribution of elements on the surface of Pu contaminated particles at the former British test site, Maralinga and Emu, Australia by Burns et al. [35, 36]. Only a small fraction of the giant particles could be analyzed. Major components of the particles from the most contaminated area were Fe and in some cases Pu, U and Pb.

Analysis of scattered and transmitted particles

During the interaction of the proton beam with the sample, some protons are elastically backscattered. In Rutherford backscattering analysis, a semiconductor detector detects scattered protons to obtain quantitative information about light elements such as C, N and O. This technique is often performed simultaneously with PIXE.

The depth profiles of light elements are determined with the elastic recoil detection technique (ERD). The forward angle scattering technique (FAST) reveals information on the quantitative analysis of hydrogen. Scanning transmission ion microscopy (STIM) is used to study local density variations in thin samples analyzed by a proton microbeam.

Recent developments aiming at total quantitative scanning analysis (TQSA) are based on the simultaneous recording of all the incoming signals in the original time sequence of events without any restrictions, followed by computerized data acquisition to obtain information available for each technique described above.

3.3.5. X ray beam techniques

Microscopic X ray fluorescence analysis

Microscopic X ray fluorescence analysis (μ-XRF) is the microscopic variant of bulk XRF. It is based on localized excitation and analysis of a microscopically small area on the surface of a larger sample by a beam of primary X rays that induces the emission of fluorescent X rays from a micro spot. The process involves the ejection of electrons from the inner shell of the atom, when sufficient energy is applied by the exciting X rays, followed by the replacement of the empty level by electrons from the outer shell while characteristic X rays, the so called fluorescent radiation, are emitted with energies corresponding to the energy differences between the two shells. The fluorescent radiation provides information on the local elemental composition of the sample. Scanning the sample with the exciting beam allows the determination of the lateral distribution of the major, minor and trace elements (provided that the flux of the primary beam is sufficiently intense) in the material.

Conventional XRF spectrometers contain an X ray excitation source (typically X ray tube, radioisotope source or synchrotron storage ring), focussing and collimating optics to produce a beam and a detecting device to measure the emitted characteristic X rays [78].

X ray excitation has several advantages over electron/particle excitation:

- It provides analysis to a greater depth within the sample than the near surface because of the higher penetrative character of X rays. Thus, layer thickness and subsurface structures can be analyzed as well;
- It is capable of performing analyses under ambient atmospheric conditions rather than in a vacuum, thereby requiring a simple sample preparation. Non-conducting materials can be analyzed without problems. X rays cause low thermal loading, allowing volatile or sensitive organic components to be Analyzed;
- XRF equipment is simple to use.

X ray beams sufficiently intense to allow sensitive microanalysis can be produced under laboratory conditions by proper focussing/collimation of the radiation originating from a microfocus X ray tube or by using much more brilliant synchrotron radiation.

Laboratory μ-XRF

In the 1980s, μ-XRF was rediscovered as a result of some basic improvements resulting in well-focussed intense μ-beams. A rotating anode X ray generator with a capillary to focus X rays from the tube to the sample was constructed. At the beginning straight capillaries were used, then conical, paraboloidal and ellipsoidal capillaries were developed that not only transported, but also concentrated the X rays through multiple reflections. The ellipsoidal capillaries also attempted to focus the radiation into a focal point.

As a result of several developments regarding the focusing system such as the use of monolithic polycapillary X ray lenses and the detection system, high intensity beams of 50–100 μm can be generated and absolute detection limits in the 1–10 pg range are obtained from thin samples, corresponding to relative detection limits at the 2–3 ppm level for elements Ca-Rb. Through the use of ellipsoidal and paraboloidal capillaries, beam sizes of 5–10 μm are attained, which are still bigger than those available by EPMA [78].

A great number of laboratory μ-XRF applications have been reported, e.g. to biological, archaeological and industrial samples. An interesting example of a nuclear application is the analysis and mapping of transition metals in MOX (mixed U-Pu oxide) fuel feed material.

Laboratory X ray microfluorescence was used at the IAEA's Laboratories at Seibersdorf to study radioactive particle composition from the French weapons test site at Mururoa Atoll. Exciting X rays of a Mo tube were focussed by a capillary that had a 10 μm diameter opening. The major elemental components of the Pu contaminated particles were often Ca, Cl, Fe, while the levels of Pu, U and Np were also above detection limit.

Synchrotron μ-XRF

Synchrotron radiation is electromagnetic radiation extending from infrared range into X ray region. The acceleration of light elementary particles produces synchrotron radiation that is much more intense (8–12 orders of magnitude) than the radiation emitted by high performance (rotating anode) X ray tubes. The latest generation (3rd) of synchrotron sources using undulators as an insertion device is ideally suitable for generating microbeams for XRF, because the radiation has not only a high intensity, a high degree of collimation, and is linearly polarized, but it is also quasi-monochromatic with tunable energy.

Synchrotron μ-XRF (μ-SRXRF) has the following advantages over electron/particle induced XRF and also over laboratory XRF using X ray tubes:

- Because of the linearly polarized nature of synchrotron radiation, the background is significantly reduced in SRXRF;
- The white spectrum produced without monochromatization provides fairly uniform elemental yields and relatively low detection limits for a range of elements and flexibilities to select the desired excitation energy;
- Using a monochromatized excitation radiation optimized (tuned) for the given element can lower the detection limit for a particular element;
- The beam coherency and its inherent collimation at the source makes it very suitable for further focusing with X ray optics, resulting in beam spot dimensions at the sample in the range of few micrometres or smaller;

- All the measurements are of non-invasive or non-destructive. However, when applying a white synchrotron beam, care must be taken especially if the sample matrix is rich in low Z elements.

Combination with other techniques:

- μ-XRF revealing the local elemental composition can be combined with X ray absorption fine structure analysis (XAFS), providing information about local atomic arrangements and electronic structure (bonding conditions and oxidation states of elements) in addition to the elemental concentrations. The energy of the excitation radiation can be continuously varied in a certain range, permitting scanning of the primary energy of the beam over absorption edges of elements of interest (see later in this section);
- μ-XRF measurements can be combined with microscopic X ray diffraction (μ-XRD), when monochromatic excitation is used, thereby providing structural data at the micrometre level that will complement compositional information**;**
- μ-XRF measurements can be combined with computed microtomography (CMT) for the visualization of local structures.

In 1995–1997 three large 3rd generation synchrotron facilities with beam lines dedicated to μ-XRF and related measurements were constructed in Europe, the USA and Japan. Janssens et al. [78] reported about the use of a 13 keV monochromatic beam of 1–2 μm for combined μ-XRF and μ-XRD measurements on individual fly ash particles. The beam flux of the capillary generated beam was about 10^{10} photon/sec/ μm^2 and in thin samples this corresponded to absolute detection levels of 5–30 attogram. The relative detection limits in organic samples for the elements Ca-Zn were in the sub-ppm level. Further improvements in the optical devices are expected to yield even smaller beams in the range of 0.2–5 μm with even higher flux densities on the sample between 10^{10} and 10^{13} photon/sec/ μm^2.

X ray absorption fine structure analysis

When the absorption of condensed matter is measured near to an absorption edge, an oscillatory behaviour is observed on the high energy side of the absorption edge i.e. the absorption fine structure. X ray absorption fine structure analysis (XAFS) is subdivided into two parts: the structure observed above the absorption edge (on the high energy side, 500–1000 eV above the edge) is called the extended X ray absorption fine structure analysis (EXAFS); that observed at the low energy side of the edge (up to about 50 eV above the edge) is called the X ray absorption near-edge structure (XANES). The first one reflects the local atomic structure arrangements and the second one is related to the electronic structure of the neighbouring atoms.

EXAFS analysis is useful for non-crystalline materials where XRD is not applicable (e.g. for amorphous materials, solutions, polymers). From the measured spectra quantitative information about the distance from the central atom to the neighbouring atoms, the coordination numbers and the atomic vibrations can be drawn, provided that the elemental composition is well known.

The XANES arises from complicated electronic processes. It is useful for the qualitative characterization of the chemical state, such as the oxidation state, of an element. Usually the XANES spectrum is compared with a reference spectrum of a sample of known chemical state. The shift of the photoelectric absorption edge is used to estimate the oxidation state of the atoms.

μ-XANES spectra of particles collected in the Chernobyl region were first determined by Salbu et al. [78] at ESRF facility. XANES proved to be a unique technique in determining oxidation states of single particles that can depend on the accident and release scenario. The spectra of the samples from the North region showed a composition close to U_3O_8. The inflexion point energies in μ-XANES spectra corresponded to oxidation state 5.0±0.5 in agreement with U_2O_5/ U_3O_8. West particles occurred as an intermediate between metallic U, U-O-Zr, and UO_2. Particles released during the initial explosion were characterized by a UO_2 core surrounded by a layer of reduced U metal, probably due to interaction with graphite. Particles characterized by UO_2 cores surrounded by U_3O_8 layer were released during the reactor fire [82, 83].

X ray microdiffraction

X ray microdiffraction (μ-XRD) is applicable for the analysis of crystalline materials. Crystal structures can be determined, the phases can be identified and defects can be characterized.

Conventional XRD studies can be made on single crystals or on powdered crystalline materials. Typically, samples are irradiated by monochromatic X rays and the diffracted radiation is detected either by photographic or electronic technique. Distances between adjacent crystal planes are calculated from X ray wavelength and diffraction angles according to the Laue or Bragg equations.

μ-XRD experiments have been performed using either continuum or monochromatic X rays produced by synchrotron sources. The number of applications of μ-XRD is increasing. Although electron diffraction technique is widely used for the characterization of crystalline materials, the synchrotron micro diffraction technique has the advantage of providing quantitative information about microcrystals. Synchrotron based μ-XRD has been used by Salbu and co-workers for characterisation of particles from a series of sites, including DU particles from Kosovo and Kuwait (see Section 4.4).

Computed microtomography

In computed microtomography (CMT), analogue to the transmission technique of computed tomography of bulk materials, the beam passes through the sample and the transmitted X ray intensities depend on the density, the thickness and the elemental composition of the sample. A series of two-dimensional data are converted to three-dimensional data by means of a back-projection algorithm, thus obtaining a three-dimensional image of the sample. The image contrast usually originates from X ray absorption. Recently a phase contrast X ray CT has been developed to enhance contrasts for weakly absorbing materials consisting of light elements. By analysing a series of phase shifts, tomograms that display the inner distribution of the refractive index were also constructed. Analysis of organic materials can be performed by this technique. μ-XAS and CMT studies were first performed on particles collected in the Chernobyl region by Salbu et al. [82, 83] using the ESRF synchrotron facility. Tomographic reconstruction of 3-D images and computerized slicing demonstrated inhomogeneous distribution of U within the particles. Microtomographic images of radioactive particles from the Chernobyl exclusion zone showed also differences in the particles' structures according to different release scenarios [83].

CMT can be also applied in X ray fluorescence mode. The measurements are carried out in a so called 'pencil' beam geometry. A parallel beam filtered back projection algorithm is used to obtain 3D reconstruction of the distribution of elements in the particle. The XRF CMT can be combined with CMT in X ray absorption mode to correct for the absorption effects and deconvolute the XRF tomograms [84].

CMT makes use of the unique properties of SR which allows the analysis of samples with micrometre-range spatial resolution and high sensitivity, without special sample preparation, in a fast and non-destructive way. A number of different CMT applications have been realized within material, medical, geological, and environmental sciences and should also be applied within radioecology.

3.3.6. Other microanalytical beam techniques

Several other microanalytical beam techniques exist that have not been used for the analysis of single particles or environmental samples. Electron spectroscopy can be mentioned here. Auger and photoelectrons are characteristic electrons. Scanning Auger microscopy (SAM) and X ray photoelectron spectroscopy (XPS often referred to as electron spectroscopy for chemical analysis or

ESCA) are surface sensitive techniques that can be applied for the analysis of surface coatings. Their environmental application is scarce. In case of SAM, problems arise from charging of the usually non-conducting samples, and low sensitivity, especially to elements of high atomic numbers. In case of ESCA, the spatial resolution is poor (about 10 μm).

3.4. MASS SPECTROMETRY

Mass spectrometry (MS) is a well-known sensitive, multielemental analytical technique often used for the determination of the elemental and isotopic composition of bulk materials. Organic compounds can also be Analyzed. Mass spectrometry is an atom counting technique with several advantages (e.g. high sensitivity, short counting times) over decay counting for the analysis of long-lived radionuclides that have sufficiently high specific masses relative to their activities. Decomposed and ionized species of the sample are dispersed by means of electric and/or magnetic fields in the electrostatic and magnetic analysers according to their specific ionic masses (mass/charge). Mass spectra are obtained by detecting the ion beams at different positions (or the same position at different magnetic fields) corresponding to different ionic masses. The major parts of mass spectrometers are the ion sources for the excitation and ionisation of the sample, the single or double focussing analysers for dispersion of ion beam and the recording device for detection of the mass distribution.

Resolution and sensitivity of MS determinations are highly dependent on the ion source and analyser type. The conventional excitation techniques of thermal and spark ionisation do not allow the determination of ultratrace amounts of elements as is required for single particle analysis. Ion sputtering used in secondary ionization mass spectrometry (SIMS) provides higher sensitivity. Extremely sensitive analyses can be performed by using more intensive ion sources e.g. plasma (inductively coupled plasma, glow discharge), accelerators and resonance ionization laser sources.

The best performance is realized by the use of intensive ion sources coupled to double focussing systems including electric and magnetic deflection fields. Quadrupole analysers are less sensitive but much cheaper. So far, various types of mass spectrometric methods have been applied to the determination of ultratrace amounts (down to femtogram levels) of long-lived radionuclides, such as secondary ionization mass spectrometry (SIMS), inductively coupled plasma mass spectrometry (ICP MS), accelerator mass spectrometry (AMS) and resonance ionization mass spectrometry (RIMS). All types of mass spectrometers have been widely applied for the determination of long-lived actinide isotopes. MS is the only method that can provide reliable information on the ^{239}Pu/^{240}Pu ratio.

AMS and RIMS are superior to other mass spectrometric techniques with respect to detection limit. So far, they are the most sensitive techniques for the environmental measurement of radionuclides with half-lives greater than about 5000 years, but their large scale application is restricted by the highly specialized instrumentation.

Ion sputtering and laser ablation can be used to determine the spatial distribution of the analyte(s) on a surface by scanning the surface area with the ion or laser beam and removing a properly thin layer of the sample that is introduced in to the ion source. Laser microprobe mass analysis (LAMMA, often called laser microprobe mass spectrometry or LMMS) and laser ablation inductively coupled plasma mass spectrometry (LA ICP-MS) offer the possibility to remove small sample areas by means of a high energy laser beam meeting the demands of a microanalytical technique. These techniques allow the study of not only bulk samples, but also single particles.

3.4.1. Secondary ion mass spectrometry

In Secondary Ion Mass Spectrometry (SIMS), a primary ion beam bombards the sample surface. A small fraction of the sputtered atoms is charged and is analyzed by a mass spectrometer as secondary ions. Since the analyzed surface is sputtered away, the depth distribution of the components can be determined in a single particle, thus heterogeneities in the particle can be revealed. The depth resolution of SIMS is about 1–2 nm. SIMS provides information about the elemental and isotope composition of the particle, organic compounds can be identified based on the detected fractions, and isotope ratios can be measured together with component imaging.

A special version of SIMS is the secondary neutral mass spectrometry (SNMS) that is also applicable for the analysis of single particles.

Grass and soil samples obtained within 150 km of the Chernobyl reactor were analyzed by glow discharge MS to determine trace elements and radionuclides in the bulk material; SIMS [85] was used to establish the location of certain isotopes. Cs-137 was incorporated in the plant, ^{129}I was found in feldspar and silicates in soil and U containing radioactive particles could be detected both in soil and grass. EPMA studies were also performed on the soil sample to identify mineral phases.

Actinide bearing particles, collected and separated from the sediment in the Yenisey River, Russian Federation, were analyzed by SIMS and actinide ratios were determined in the single particles assuring sensitive measurements free from the interfering effect of natural actinides also present in environmental samples [67].

Jernstrom et al. [86] also used SIMS for the characterization and source term assessment of radioactive particles from the Marshall Islands.

3.4.2. **Inductively coupled plasma mass spectrometry**

The inductively coupled plasma ion source (ICP) has been interfaced to different mass analyzers such as the linear quadrupole, the time of flight, the Fourier transform ion cyclotron resonance and the electric/magnetic sector field ones. In inductively coupled plasma mass spectrometry (ICP-MS), aliquots of liquid samples are introduced into the plasma and the positive ions are separated by the mass spectrometer. Since plasma is used as ion source, the sensitivity and the accuracy of the measurements have been improved significantly compared to conventional mass spectrometry using thermal or spark ionization techniques. Thus, ICP-MS became one of the most powerful methods in analysing trace amounts of stable and radioactive isotopes, and the determination of isotope ratios. The introduction of double focusing sector field instruments (ICP-SF-MS) in the late 1980s improved the mass resolution, several spectral interferences could be resolved, lower background was achieved, ion transmission was improved, and consequently the sensitivity was increased and ultratrace amounts of elements could be analyzed. Typical sensitivities for ICP-SF-MS are as low as a few femtograms.

However, analyzing isotopes below the pg to ng range is problematic. ICP-MS has relatively low abundance sensitivity (1–10 ppm), spectral interferences are produced by polyatomic species, peak tailings in the mass spectra are significant, and the instrument background is affected by memory effect. All together, these problems result in reduced sensitivity, especially in the presence of 'neighbouring masses'. For example, the detection limit for ^{239}Pu is significantly reduced if ^{238}U is present in the sample, due to the tailing of ^{238}U peak and the presence of $^{238}UH^+$ species originating both from the sample and the blank. In order to minimize the problems, the analyte has to be well separated from the interfering elements during sample processing. In general, desolvating equipment can be used for sample introduction to reduce the probability of hydride formation, and polyatomic species can be removed by using reaction/collision cells. In the case of ICP-SF-MS, a high resolution operation mode should be used. The memory effect can be reduced by proper cleaning of the sample introduction system.

ICP-SF-MS was successfully applied for the determination of Pu isotopes and isotope ratios, for the analysis of ^{237}Np, ^{99}Tc, ^{129}I, ^{90}Sr, ^{135}Cs, ^{137}Cs, ^{241}Am, ^{226}Ra, U and Th isotopes in nuclear and environmental samples, usually after radiochemical separation of the analyte element [87–89].

Lind [89] used ICP-MS for the determination of the U and Pu isotope ratios in the particles originating from the nuclear weapon accidents at Palomares, Spain in 1966 and Thule, Greenland in 1968.

Eriksson et al. [90] studied the nuclear fingerprint of the Thule accident using high resolution ICP-MS (HR-ICP-MS) to determine the isotopic and element ratios and the masses and activities of U, Pu and Am in five particles isolated from sediment.

LA-ICP-MS is a sensitive, direct analytical technique for the quick determination of isotopes and isotope ratios of solid surfaces. It has been applied as an imaging mass spectrometric technique. Single zircon ($ZrSiO_4$) particles were analyzed by LA-ICP-MS by Becker [88]. U and Pb isotopes were detected to calculate the age of the Precambrian Baltic Shield from the single grains. U isotope ratios were determined by the same technique in single UO_2 particles of 1 µm size or less. The result demonstrated an enrichment of U in the particles compared to the isotopic composition in natural background.

3.4.3. Accelerator mass spectrometry

In accelerator mass spectrometry (AMS), high sensitivity is achieved by combining the high sensitivity of mass spectrometry with a high level of discrimination against polyatomic/molecular interferences: two mass spectrometers are combined with a particle accelerator that serves as a molecular dissociator. Sample atoms are ionized efficiently in an ion source producing negative ions that pass a magnetic spectrometer. Then they are accelerated to high energies with a particle accelerator and turned into positive ions that are separated with a second mass spectrometer containing both an electrostatic filter and a magnetic separator.

Finally, the separated positive ions (as individual isotopes) are counted using particle detection methods developed for particle and nuclear physics (e.g. Faraday cup, ionization chamber, silicon detector). The negative ion sources are typically Cs sputter sources, and the accelerators operate at a voltage of 0.3 to 11 MV. AMS was traditionally developed for the measurement of light elements such as ^{14}C. With some modifications it became applicable for elements as heavy as the actinides.

AMS has been used for the measurement of various U, Pu and Ne isotopes and isotope ratios, and for the determination of ^{226}Ra, ^{228}Ra, ^{129}I, ^{99}Tc etc. in environmental samples after radiochemical sample pre-treatment. AMS offers a sensitivity that can approach 0.1 femtogram and the advantage of immunity to polyatomic/molecular interferences. AMS is the method of choice for those applications where small amounts of radionuclides have to be analyzed in the presence of large amounts of carriers or 'neighbouring interferences', e.g. for the determination of $^{236}U/^{238}U$, $^{129}I/^{127}I$ ratios, etc. [91, 92].

AMS has been used for the analysis of various long-lived radionuclides and the isotope ratios of $^{240}Pu/^{239}Pu$ and $^{236}U/^{238}U$ in environmental samples originating from different regions affected by radionuclide releases from spent fuel reprocessing plants, such as facilities at Mayak and Krasnoyarsk in Russian Federation and Sellafield in the UK [15, 89, 93–97].

AMS offers the necessary sensitivity for the determination of $^{236}U/^{238}U$ ratio in environmental samples and in depleted U probes originating from the armour-piercing shells used in the Iraq and Kosovo wars [24, 96]. Elevated levels of ^{236}U proved that the U containing material had been reprocessed [96]. This is an important issue for safeguards purposes as the isotopic ratios can serve as a sensitive fingerprint. Although the application field of AMS has grown rapidly, its advantages in the analysis of radioactive particles have not yet been fully implemented.

3.4.4. Resonance ionization mass spectrometry

Selective determination of extremely small amounts of long-lived radionuclides and their isotope ratios can be performed by atom counting using selective laser based resonance ionization in combination with conventional mass spectrometry - Resonance Ionization Mass Spectrometry *(RIMS)*. Due to the elemental selectivity of laser excitation and ionization and the mass selectivity of the mass spectrometer, isobaric interferences are suppressed and high to ultrahigh isotopic selectivity is achieved. High detection efficiency results from the high cross-sections for optical excitations. RIMS has the advantage of being a fast technique if sample preparation time is not included.

Typically, analytes are concentrated on a filament, and neutral atoms in the gas phase are produced by thermal evaporation or resistive heating. For the determination of the spatial resolution of the analyte, e.g. for radioactive particle analysis, laser ablation or ion sputtering should be applied offering a resolution down to micrometre size. Gas phase atoms are selectively excited and ionized by properly tuned laser light (ultraviolet, visible or infrared) in several steps. Pulsed laser systems, solid state laser systems, tuneable continuous wave (cw) lasers, as well as diode lasers are used. Pulsed lasers are combined with time-of-flight mass spectrometers, while quadrupole, magnetic sector field or double focussing magnetic/electric sector field mass spectrometers are attached to the cw-lasers [98].

RIMS offers extremely high elemental (molecular) selectivity, high isotopic selectivity, and high optical isotopic selectivity, resulting in an overall isotopic selectivity of about 10^{12}. The detection limit of RIMS lies in the range of 10^6 atoms per sample which corresponds to fentogram amounts of many elements and long-lived isotopes.

RIMS can be applied for the ultrasensitive determination of U isotopes including ^{236}U, Pu isotopes, ^{89}Sr/^{90}Sr, noble gases e.g. ^{85}Kr, and ^{99}Tc, ^{41}Ca in environmental samples after chemical processing. RIMS has been used for the analysis of the isotope ratios of Pu nuclides in different environmental samples including dust samples from Germany, soil samples from the Chernobyl area, and sediment from the Mururoa Atoll (see Erdmann [98]).

There is a great interest for the application of RIMS in radioactive particle analysis, but a routine procedure has not yet been implemented. Coupling RIMS with atomization techniques that allow high lateral resolution, such as laser ablation/desorption or ion beam sputtering, is presently under investigation.

3.4.5. Laser microprobe mass analysis

In laser microprobe mass analysis (LAMMA), a high power density pulsed laser beam is used to evaporate and ionize a small area of a sample. Sample surfaces can be scanned by the laser beam. The ionized part of the evaporated material consists of positive and negative charged elemental and molecular ions that can be analyzed by two methods, i.e. time of flight MS or Fourier transform MS.

The time of flight mass spectrometry (TOF MS) separates the ions with different mass-to-charge ratios according to their flight times. Depending on the polarity of the electric field, positive or negative ions are detected. Commercially available TOF LAMMA devices have limited sensitivity and resolution. The technique is suitable for the analysis of elements. For the determination of organic compounds, better mass resolution is required. Improvements have been achieved with the application of resonant positioning. Spatial resolution of the method is good, about 1 μm. For the processing of great amounts of individual spectra, computer aided methods have been introduced based on pattern recognition or library search.

In on-line LAMMA, aerosol particles are directly analyzed, measuring the particle size using the scattered laser beam, while mass spectra are determined by the time-of-flight LAMMA. Aerosols are introduced directly into the mass spectrometer with a nozzle. The aerosol beam intercepts the helium-neon laser beam giving rise to scattered radiation from each particle that is included in the analysis of the particle size distribution. The scattered signal triggers an excimer laser that vaporizes and ionizes the fragments. A complete mass spectrum is determined that corresponds to a single particle ablated by a laser pulse. On-line LAMMA has the great advantage that samples are analyzed in-situ without risk of contamination or decomposition, and with reduced losses in volatile components due to the short residence time of the sample in vacuum before ionisation (<1 ms).

Fourier Transform Laser Microprobe Mass Spectrometry (FT LAMMA) has better mass resolution and higher accuracy than TOF LAMMA. Sample ionisation can take place in an ion cyclotron resonance cell (also in an external ion source followed by introduction of the ions into the cell). Ions are brought into resonance with the frequency of an oscillating field, pick up energy and become coherent ion packages that are detected. Fourier transformation of the time-dependent signals results in a frequency spectrum that can be scaled into conventional mass spectrum by calibration. In FT

LAMMA a better mass resolution is achieved, the detection limit for elemental ions is about 10^8 atoms within a microvolume and the minimum spatial resolution is about 5 μm, somewhat worse than for TOF LAMMA.

3.5. COMPARISON OF SOME ELEMENTAL MICROANALYTICAL TECHNIQUES

A brief comparison on the general characteristics of a number of microanalytical techniques, according to Janssens [78], is given in Table 4. The capabilities of various analytical techniques for determination of Pu isotopes, as evaluated by Xiaolin Hou et al. [99], are presented in Table 5.

TABLE 4. COMPARISON OF SOME MICROANALYTICAL TECHNIQUES [74]

Technique	Projectile, Quantum energy (keV)	Beam Size, (μm)	Beam Penetration, (μm)	Minimum Detection Limit (ppm)	Destructive	Calibration
EPMA	e^-, 5–50	<0,1	1–10	1000	No	easy
μ-PIXE	P^+, 2–3× 10^3	0,3–5	5–100	1–100	yes/no	easy
μ-SRXRF	X, 2–80	0,7–10	100–1000	0,1–100	No	easy
SIMS	M^+, N^-, 10–30	0,5–10	<0,1	<1	yes	difficult
LAMMA ICP	photon	20	10	0,5–5	yes	intermediate

TABLE 5. COMPARISON OF RADIOMETRIC AND MASS SPECTROMETRIC METHODS FOR THE DETERMINATION OF ISOTOPES OF PLUTONIUM [99]

Sample	Detection method	Nuclide	Detection limit	Separation time	Counting time
Environment	X ray spectrometry, underground counting	^{239}Pu ^{240}Pu	4.4 mBq 2.0 mBq	3–5 days	57 days
Environment	α spectrometry	^{239,240}Pu, ^{238}Pu	0.05 mBq	2–3 days	3 days
Environment	α spectrometry	^{239,240}Pu, ^{238}Pu	0.02 mBq	3–4 days	5 days
Environment	LSC	^{241}Pu	11 mBq	2–3 days	5 days
Environment	α spectrometry	^{241}Pu (via ^{241}Am)	0.5 mBq	3–5 days (13 years)	3 days
Urine	TIMS	^{239}Pu ^{240}Pu ^{241}Pu	1.4 μBq 0.9 μBq 0.4 mBq	2–3 days	20–30 min
Environment	ICP-SF-MS	^{239}Pu ^{240}Pu ^{241}Pu	21 μBq 14 μBq 11.9 mBq	3–4 days	20 min
Environment	RIMS	^{239}Pu ^{240}Pu ^{241}Pu	10 μBq 30 μBq 20 mBq	2–4 days	1–2 hours
Sea water	ICP-SF-MS	^{239}Pu ^{240}Pu	0.78 mBq/mL 3.6 mBq/mL	3–4 days	20 min
Urine	AMS	^{239}Pu	0.5 μBq	2–3 days	20–40 min

3.6. ACTIVATION ANALYSIS

Although activation analysis has proved to be an excellent non-destructive, multielemental analytical technique of extremely high sensitivity for bulk analysis, it is rarely used as a microanalytical method, because the beam size is usually large. Sufficiently small-sized neutron beams cannot be produced for the purposes of sample scanning. On the other hand, charged particles can be well-focussed and using particle beams charged particle activation analysis can be applied as a surface analytical technique where prompt gamma radiation can be detected.

During the interaction of protons with the nucleus of certain elements, prompt gamma rays are generated that can be detected with Ge semiconductor detectors. With particle-induced gamma emission (PIGE) several elements have been analyzed e.g. F, Na etc.

3.7. INFRARED SPECTROSCOPY

In infrared spectroscopy (IR), the specific absorption of IR radiation in the wavelength range of 2–200 μm is measured. As a result of IR radiation absorption, the quantised vibrational states of the molecule or the crystal are changed giving rise to changes in the dipole moment in the structure. By means of IR spectroscopy isolated vibrations assigned to chemical bandings, weak molecular interactions as well as coupled vibrations due to condensed structures and strong solid-state interactions can be studied. Thus, IR spectroscopy can be successfully applied for the structural analyses of both organic and mineral materials.

IR spectroscopy was originally developed for the analysis of bulk sample composition. It was also coupled to other analytical techniques such as chromatographies (gas, liquid) and thermogravimetry. Fourier transformation (FT) IR microscopy offers the possibility of analysing individual particles with diameters of <5 μm. To isolate the areas of the sample to be analyzed, knife-blade apertures are applied. This image masking technique on the FT IR microscope is quick and accurate.

Micro FT IR spectrometry has been applied for the analysis of environmental particles, but investigations on radioactive particles have not been yet reported.

4. CHARACTERIZATION OF RADIOACTIVE PARTICLES

Radioactive particles can be characterized and classified according to the following properties [12, 15]:

- Particle size, shape and appearance; particle size distribution for a set of particles or size (diameter) of individual particles, including aerodynamic diameter for airborne particles as well as shape and colour;
- Elemental composition including the 2D and 3D distribution of radionuclides and stable elements within the bulk particle and on surfaces;
- Structures such as crystalline and amorphous phases;
- Valence and oxidation states, surface charge properties.

When impact assessments are made for areas contaminated with radioactive particles, information is needed not only on the particle densities/frequencies and their spatial and depth distributions, but also on individual particle characteristics influencing weathering rates and remobilisation of associated radionuclides [12].

Radioactive particles can be classified according to their source and their formation mechanisms [12, 15]. In the following sections, the major types of radioactive particles are discussed; those originating from nuclear weapons tests, reactor accidents including the Chernobyl accident, conventional destruction of nuclear weapons, the use of DU in ammunition, authorized and accidental releases from nuclear facilities, dumped nuclear wastes and some other sources of contamination.

4.1. CHARACTERIZATION OF RADIOACTIVE PARTICLES ORIGINATING FROM NUCLEAR WEAPONS TESTS

As discussed in Section 2, a great number and a variety of nuclear weapons tests were conducted around the world including aboveground, underground and underwater tests, as well as peaceful nuclear explosions. Atmospheric tests were of major concern regarding releases of radioactive material both in the near field and far away from the test sites causing local, regional and global environmental contamination [1]. In this section, the properties of radioactive particles originating from atmospheric weapons tests are discussed in more detail. It should be noted that most of the literature cited were published in the 1960–1970 period. Although only quite simple measurement techniques were available, quite extensive knowledge was attained.

According to Adams (cited by Kern [40] and Gross [100]), four types of radioactive particles are formed in the fireball during the detonation of nuclear bombs:

1. Type (1) particles are formed by condensation of vapours of fission and activation products and the bomb materials including the fissionable materials as well as other construction materials of the bomb. The diameter of the particles formed by this mechanism is less than 1 μm.
2. Type (2) particles are formed by precipitation of the molten components of the bomb and materials that are sucked into the fireball e.g. soil, coral rocks, and metal stands used to hold the bomb before explosion. Droplets formed in this process contain stable elements such as calcium oxide, silicon dioxide or iron oxide as matrix component and several other chemical compounds. Typical particle sizes are large, in the range of 0.2–2 mm. Particles have a spherical shape. The inner part of the particle is more or less homogeneous, and changes in the surface layer occurr as a result of adsorption.
3. Type (3) particles are formed from solid or partially molten components of the ground. On the surfaces both condensed gaseous fission products and adsorbed small radioactive particles of type (1) can be found. Such particles could have irregular shapes.
4. Agglomerates of radioactive particles of types (1)–(3).

According to Crocker et al. [4] the particles formed are device and shot dependent. Spherical particles (type 1 and 2) are formed at high altitudes, while ground detonations produce vitrified particles with inclusions of soil compartments (type 3).

4.1.1. Radioactivity of the particles

Radioactive material in particles originates from the fissionable material itself (U or Pu) as well as the production of fission products according to the fission yields of the major fission processes taking place in the detonation. The major fission processes are the slow neutron induced fission of ^{235}U, ^{239}Pu or ^{232} U, and the fast neutron induced fission of ^{238}U or ^{232}Th in different types of nuclear and thermonuclear devices. In addition to fission products, a number of radionuclides are produced by nuclear transmutations, including substantial amounts of ^{239}Pu and other transuranium elements. Other radionuclides are produced by neutron activation of stable elements of the bomb and the surrounding materials e.g. components of the atmosphere, seawater or soil depending on the location of the explosion.

Radioactive material can coat the surface of existing particles or can act as the carrying matrix, and the radioactivity can be proportional to d^2 or d^3 (d = particle diameter), respectively, depending on the formation process. Intermediate distributions are also possible if the two kinds of particles are mixed or if other particle formation mechanisms occur.

4.1.2. Mechanism of radioactive particle formation

Adams [referred to in [40] and [100]) has discussed the processes taking place in the fireball assuming that the major chemical components iron and oxygen are in gas phase at the moment of detonation. When the temperature in the fireball decreases, condensation processes take place parallel to the decay processes of the freshly produced radionuclides. Condensation is rapid; in some seconds iron oxide will condense, while relatively small amounts of fission products will condense sometime later. This mechanism is only valid for detonations where matrix components other than iron are present.

Distribution of radioactive material in the particles depends on the temperature-time history of the particle formation in the fireball, and on the nuclear and the chemical properties of the radionuclides.

This phenomenon called primary fractionation has been studied in detail by several authors [46, 100, 101]. It implies that the isotope ratios in the particles deviate from those theoretically determined from nuclear production and decay yields. The fractionation of fission products occurs due to the fact that the fission products, which are formed in the same decay chain, have different half-lives and chemical-physical properties/volatilities. Among the fission products there are gases e.g. noble gases which, though short-lived, exist sufficiently long so that their daughter nuclides are formed late in the life of the fireball, after the condensation processes of the debris have already begun or terminated. Thus, the daughter nuclides, even the non-volatile ones, will be depleted in the particles. Disequilibria may also occur because the different nuclides condense from the fireball at different temperatures. The more volatile elements, which condense last, are often deposited on the surfaces of small particles, which settle more slowly.

The time interval between detonation and particle formation can be determined from the measured fractionation factors of the different fission products in the radioactive particles. The interval depends on many variables that influence the temperature in the fireball and the speed of condensation e.g. the type and yield of the bomb, the conditions of detonation (air burst, land surface burst etc.). For example, Mamuro [51, 101] calculated this time interval to be 30–40 sec from studies of radioactive particles originating from the 3rd Chinese weapons test that was an air burst explosion, and a time interval of 50–100 sec in case of the 5th Chinese testing that was a land surface burst.

4.1.3. Particle size

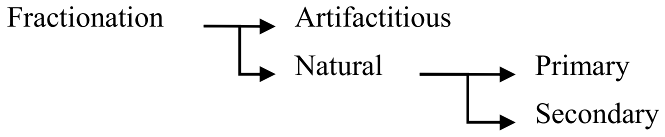
Particle size and morphology are dependent on the type of explosion. Near-surface detonations produce large glassy particles that are highly radioactive, as well as log normally distributed particles of smaller size. Bursts that take place at high altitudes in the atmosphere produce smoke like particles of small size that remain suspended for considerable periods of time. Larger particles are the result of coalescence of smaller ones.

Particle size and shape determine their transport behaviour. Depending on the height of the burst and the explosive yield, particles are divided into three groups. Larger particles will deposit close to the site of detonation within some hours. Medium size particles are dispersed into the troposphere and fallout (washout) at a certain distance may occur after some days depending on meteorological conditions.

The smallest particles can penetrate into the stratosphere and can deposit worldwide, sometimes circling around the globe several times over a period of some months. The circling period was determined by Thein [49] and later by Chen [102]. The tropospheric fallout tends to be distributed in bands at the latitude of detonation, while the stratospheric debris distributes globally. During particle transport another type of fractionation occurs that is different from the radionuclide fractionation taking place in the fireball. Depending on their aerodynamic properties, particles of different size and shape will have different transport ranges.

4.1.4. Fractionation

The term ‘fractionation’ in a broad sense was clearly defined by Freiling [103] as any alteration of radionuclide composition occurring between the time of detonation and the time of radiochemical analysis, which causes the debris sample to be non representative of the detonation products taken as a whole. He classified the fractionation effect according to the types of processes involved as follows:



Natural fractionation begins with the condensation of radioactive and inert material from the fireball, some radionuclides being preferentially taken up by the condensate. Further separation of the condensate occurs according to size, density, and shape under the influence of wind, gravity, and cloud turbulence. The fractionation taking place through these processes is called primary fractionation. Secondary fractionation occurs through contact of the debris with radioactively inert surroundings e.g. through leaching by water, adhering of small particles to available surfaces. Artifactitious fractionation can be induced by sample-collection processes or by faulty analytical processes.

A fractionation factor was defined by Edvarson [99] in the following way:

$$f_{A-95} = \left(\frac{N_A}{N_{(Zr+Nb)95}} \right)_{\text{exp.}} / \left(\frac{N_A}{N_{(Zr+Nb)95}} \right)_{theor.}$$

where N_A is the activity of the nuclide in question. The first and second brackets contain the experimental and theoretical values respectively, as obtained from known fission yields. The ^{95}(Zr-Nb) couple is selected as reference because they behave very refractory.

By determining fractionation factors for different radioactive particles, conclusions can be drawn about the particle formation mechanism, the detonation process and also the type of bomb. Thus the source of radioactive particle emission can be identified (see e.g. Mamuro [51, 101] or Grüter [42]).

4.1.5. Radioactive particles originating from global fallout

Major characteristics of some radioactive particles originating from worldwide fallout are summarized in Table 6. Most of the measurements were performed in the 1950s and 1960s following aboveground explosion tests.

Some of the measurements were performed in the 1970s when, despite of the non-proliferation treaty, France and China continued the atmospheric weapons tests. Intensive long-term investigations on environmental radioactive particles were carried out in some laboratories, especially at the Radiation Centre of Osaka Prefecture, Japan and at the Chemistry Department of University of Arkansas in Fayetteville, USA. Although the radioanalytical techniques available at that time could not be compared with those available today (no semiconductor detectors nor electron microscopes), valuable results were produced with respect to particle identification and characterization and especially in understanding processes involved in particle transport and environmental contamination.

It was recognized quite early [102, 49] that particles from bombs of high explosion yields could reach the stratosphere and that particles were slowly deposited after circling the Earth several times. The fractionation phenomenon was also explained in detail based on complex spectra of fission products mixtures, for instance using simple scintillation detectors. Freiling [103], Mamuro [51, 101, 105], Rao

[53], Baugh [106] and their colleagues helped explain how condensation proceeds in the fireball in time intervals of a few seconds and later during transportation, fallout, rainout and washout.

Without electron microscope it was hard to determine the exact size of particles. Indirect methods were used, and most often particle sizes were calculated from the activity of the particles assuming that the relationship was linear, which seldom could be valid. The specific activity of the particles depends on their composition and is significantly reduced when inactive materials are involved during particle formation, as in the case for land-surface bursts relative to air bursts, as was recognized by Mamuro [51, 101]. Following the atmospheric tests, a series of radioactive particles have been identified [100–110].

Sisefsky [56] made valuable efforts to calibrate the autoradiographic measurements. Based on radioactive particles originating from worldwide fallout it could be established that the particle diameters were in the range of some microns, in good agreement with theoretical assessments. Nearly all particles found in Europe both at higher altitudes (e.g. above Sweden [103, 108] and in air filters collected in Norway (Salbu, pers. comm.)) and on the ground (e.g. in Germany) were smaller than 10 µm. Typical values measured in Fayetteville, USA after various Chinese tests were similar [56, 49, 103], while particles detected and measured in Japan after the same Chinese tests were significantly bigger, 5–30 µm in diameter. This is probably explained by the shorter distance between Lop Nor and Osaka. Some giant particles were occasionally detected such as a 34 µm particle in Fayetteville, USA and a 64 µm particle in Münster, Germany. No aerodynamic explanation could be given for how those particles could be transported from the estimated long distances of the test sites.

Data about the composition and the structure of radioactive particles identified during the times of the atmospheric explosions are, however, very scarce. Analytical techniques had not sufficient sensitivities to measure microscopic amounts. Elemental composition of particles was determined for the Münster sample that was collected in 1962, but the analyses were performed in 1985 by means of XRF techniques revealing the presence of the non-radioactive components Ca, Fe, Ni, Cu, Zn, and U. Posterior studies of old samples with new techniques, as demonstrated in the present document, should further develop our understanding of radioactive particles, their formation, characteristics and environmental impact.

4.1.6. Radioactive particles originating from local fallout at weapons test sites

Table 7 presents a short review of the characteristics of radioactive particles originating from the local fallout of different types of weapons and safety tests. Major surveys have been performed more recently on several former test sites including the British, the American, the French and the Soviet sites. In some cases preliminary cleanup actions had also been conducted, although most of the areas are still heavily contaminated, especially by Pu, U and Am.

Thus, much higher activities, different isotope composition and larger particles are expected to contaminate the near-field areas than in areas further away from the explosion sites. Particles on the former test sites are sometimes huge. Particles which have diameters above 2 mm are referred to as fragments, and not particles, and they are usually characterized by high radioactivity.

Recently, separated individual radioactive particles originating from different test sites have been studied by various research groups using sophisticated micro- and radioanalytical techniques. One of the major goals of the present CRP was to characterize such particles. In the following paragraphs present a short review about the level of contamination at the given test sites and a summary of results of the characterization of single particles.

TABLE 6. CHARACTERISTICS OF RADIOACTIVE PARTICLES ORIGINATING FROM WORLD-WIDE FALLOUT

Reference	Sampling location & time	Weapons test location & time	Number of RPs	RP density RP/1000m^3	RP diameter µm	Activity/RP Bq
[104]	Sweden 1957–1958	Worldwide	7	1–24	>0.2–1.2	-
	Air: altitude 8–12 km	Aug 1957–Feb 1958	4	0.3–3	>1.4–1.9	0.1–3
			11	0.01–12	>0.4–5	-
[56]	Sweden 1958	USSR/Novaya Zemlya	950		0.1–5	0.001–35
	Air: strato. + troposphere	Sep+Oct 1958				
[40], [108]	Germany	Worldwide			<10	<40
	1958–1959	1957–1958			<3	
[109]	Japan/Osaka Nov. 1961	USSR; Sep 1961	>50		7–14	
[105]	Japan/Osaka Nov. 1961	USSR; Oct 1961	>50		8–14	200–3000
[53]	Japan/Osaka	China; May 1965	20		5–15	
[106]	USA/Fayetteville	China		1–30	2–4	0.5–35 Bq/1000m^3
	May–Aug 1966; Air filter	May 1966				
[102]	USA/Fayetteville	China		1–30		
	May–Aug 1966; Air filter	May 1966				
[101]	Japan/Osaka	China	21		8–14	
	May 1966; Air	May 1966, Air burst				
[26]	USA/Fayetteville +	China	3		5–7	15–40
	Japan/Osaka May 1966, Air	May 1966, Air burst	12		6–16	20–500
[51]	Japan/Osaka, Dec. 1966	China	17	>150/m^2	19–28	100x lower than in air burst
	Air	Dec 1966, Land burst				
[110]	Finland 21–26, Dec 1966	USSR/Semipalatinsk				
	Air filter	Underground, Dec 1966				
[49]	USA/Fayetteville			0.5–1	>2–3	
	28 Dec 1967–24 Jan 1968; Air filter			3–100	<1–2	
[107]	USA/Fayetteville	China; Troposphere: Jan 1972		4–200	0.1–5	
	Aug 1972	Stratosphere: Mar 1972		1–30	0.1–7	
	Air			10	5–7	
				10–40	0.1–1	
[42]	Germany/Münster	USSR/Novaya Zemlya	1		34	
	1962	Oct 1961	3		30–65	

Maralinga, Australia

According to the contamination level, Burns [7] divided the Taranaki site into 3 regions: the highly contaminated 'A' region with 33 fragment m^{-2}, the medium contaminated 'B' region with 7 fragment m^{-2} and the least contaminated 'C' region with 2 fragment m^{-2}. The ^{241}Am activity of each fragment exceeded 2 kBq. One of the biggest fragments found at Taranaki/Maralinga was a 25 × 12 cm steel plate containing 7 GBq of ^{239}Pu [6].

After the removal of most of the big fragments, the attention was turned to radioactive particles as discussed in the paper of Burns et al. from 1995 [35]. Particle size distribution measurements were carried out at the Taranaki site to determine the inhalable fraction of the particles. The common conclusion was drawn that the activity distribution of e.g. ^{241}Am was quite different from the mass distribution, with the inhalable fraction substantially enriched in activity.

Burns [35] carried out resuspension experiments and determined the activity median aerodynamic diameter (AMAD). He found that the diameter was reasonably consistent at different sites at Taranaki, with an average of about 6 μm. In accordance with the measurements of Simon et al. [111] at Rongelap, more than 99% of the activity was associated with particles which were smaller than 150 μm. The smallest fraction studied (<40 μm) contained the highest activity. Future investigations should be extended to small particle sizes. Some 'giant' particles (<1 mm) from Taranaki were analyzed by PIXE and the results showed that those particles did not contain the typical ground elements, Ca and Sr. The major identified components were Fe and Pu.

Marshall Islands

Pu contaminated soil from the Marshall Islands was studied to determine the spatial and volumetric distribution of contamination in macroscopic (grams) and microscopic masses (<1 mg) using alpha spectrometry and nuclear track detectors by Simon et al., 1995 [111]. Samples were taken from surface soil on Rongalap Island on grids with distances between 40 and 200 m. The concentration of transuranic radionuclides (^{239,240}Pu and ^{241}Am) increased with decreasing particle size. Significant heterogeneity of transuranium elements was observed on both the macro- and microscopic scale.

Pu-containing particles stemming from Runit Island soil on Enewetak Atoll were separated and characterized by non-destructive microanalytical techniques by Jernström et al. [86] and Hamilton et al. [112]. Distribution of the elements in the particles was determined by synchrotron radiation based SR-μ-XRF, while morphology and elemental composition were studied by SEM-EDX and WDX, and SIMS was used to examine particle surface. Two types of Pu-rich particles were identified according to elemental composition. Type 1 particles were smaller with mainly Pu as matrix, whereas in Type 2 particles Pu was heterogeneously distributed in a Si- and O-rich matrix forming larger glass-like structures. No U was detected in any of the particles.

Type 1 particles were identified as fuel fragments of the initial nuclear weapon material. This is supported by the fact that no traces of other elements of the Pu weapon structure were found, and that the particle matrix differed from the calcareous soil of Runit Island. The low ^{240}Pu/^{239}Pu atomic ratio (<0.065) and the low fission product content in all particles indicated no or minor fission of the bomb material, which was probably from the Quince safety test. Type 2 particles appeared to contain trace amounts of ^{137}Cs suggesting that these particles formed during a fission (low yield) event, most probably from the Fig low yield test.

Both the Quince and Fig tests were performed on Runit Island in 1958. The ^{241}Am/^{239}Pu atomic ratio (3.7×10^{-3}) in the particles indicated they were of similar age. The SEM image, the EDX spectrum and the Pu distribution map of a 'plain' Pu particle (a) separated from Runit Island soil are shown in Figure 1. The particle area was 2640 μm^2.

Nevada, USA

Hot spots and localized heterogeneities reflected the presence of radioactive particles in soils at the Nevada, USA test site [3, 4, 113]. A large variety of fused and partially fused Pu-containing particles, vesiculated particles and large agglomerates differing in colour, specific activity, density and magnetic properties have been identified.

According to Crocker et al. [4], the particle size distribution depended on device and shot conditions; spherical and small-sized dense particles with uniform distribution of activities were obtained from high altitude shots e.g. similarly to the particles collected in the Semipalatinsk test site, while in ground surface shots large irregular shaped particles with lower density and specific activities were formed. These particles contain soil components. Analysis of individual radioactive particles originating from the Nevada site by advanced analytical techniques has not been reported.

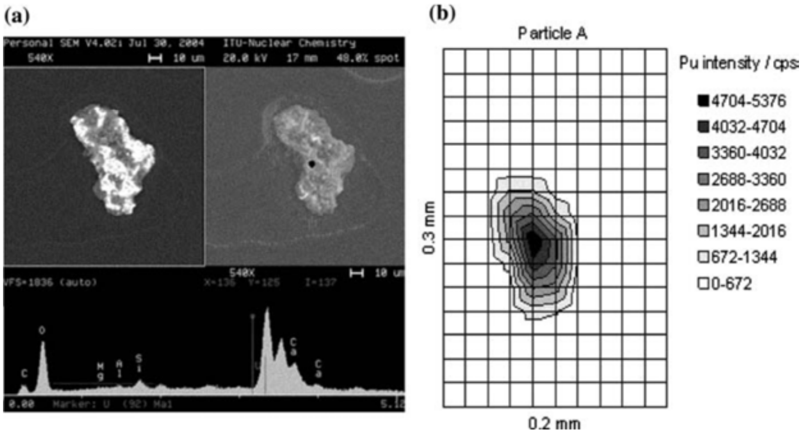


FIG. 1. SEM images and EDX spectra of a particle from Runit Island [86, 188]. The two adjacent images represent the same particle. The left-hand image set contains two SEM images and EDX spectrum. The energy range of the EDX spectra is between 0 and 5.12 keV. The small black spot on the particle images marks the position where the EDX spectrum was measured. The contour plot on the right side shows the Pu Lα XRF intensity distribution in the corresponding particle.

Mururoa and Fangataufa Atolls, French Polynesia

The IAEA carried out a survey on the atolls of Mururoa and Fangataufa in 1998 [5, 114]. First of all, bulk radioactivity was determined and recently some 'giant' radioactive particles of 150–650 μm sizes have been analyzed by μ-XRF technique. The main components of the samples were calcium, iron, chlorine, and sometimes strontium. U, Pu as well as Np could be detected by X ray method. The results indicate the presence of soil components in the radioactive particles from Mururoa.

A single particle from Mururoa Atoll was examined by microtomography by Eriksson et al. in 2005 [84]. The particle was separated from coral sediment and studied using the X ray microtomography spectrometer designed by IAEA Laboratories at Seibersdorf [114] and set up at the ANKA synchrotron facility, Karlsruhe (Fig. 2). The particle was Pu-rich and embedded in a coral matrix on one side. Results suggest that the merging of Pu with the matrix occurred during the nuclear test explosion. Besides Pu, the particle contained strontium. Microtomographic studies revealed that Pu and Sr were not homogenously distributed in the coral based particle.

TABLE 7. CHARACTERISTICS OF RADIOACTIVE PARTICLES ORIGINATING FROM LOCAL FALLOUT AT WEAPONS TEST SITES

Ref.	Sampling location & time	Weapons test location & time	Number of RPs or fragments	RP density RP/m^2 or F/m^2	RP size	Activity/RP (Bq/RP) or (Bq/F)
[6]	Taranaki	Maralinga, Emu	1 F		25 × 12 cm	7.0 × 10^9/F
	7 test sites	Major tests: 1956–59	100000F		-	Am >1E5
	32 km zone	Safety tests: 1960–63				
	Soil, fragments	Cleanup: 1968				
	1984 survey					
[7]	Taranaki	Maralinga, Emu	F	A region: 33	Visible	^{241}Am>2000/F
	7 test sites	Major tests: 1956–59	F	B region: 7	Visible	^{241}Am>2000/F
	32 km zone	Safety tests: 1960–63	F	C region: 2	Visible	^{241}Am>2000/F
	Soil, fragments	Cleanup: 1968	F	A region: 3	Visible	^{241}Am>20000/F
	1984 survey		F	B region: 0.6	Visible	^{241}Am>20000/F
			F	C region: 0.1	Visible	^{241}Am>20000/F
			3E6F		-	^{241}Am>2000/F
[36]	Taranaki	Maralinga, Emu	5 RP		< mm	Pu: 30–4500/RP
	1500–500 yards from	Major tests: 1956–59	40 RP		0.1–1.6 mm	Pu: 600–330 000/RP
	firing sites	Safety tests: 1960–63	77 RP		< mm	Pu: 400–194 000/RP
	Soil	Cleanup: 1968				
[35]	Taranaki	Maralinga, Emu	4 RP		< mm	-
	18 km away along plume	Major tests: 1956–59	1 RP		36 µm	
	Soil, resuspension	Safety tests: 1960–63	54 RP	(1100*)	6–500 µm	Am: 15/RP
		Cleanup: 1968				-
[111]	Rongelap	Rongelap/Marshall Islands	4 size fractions of 4 RP	$<6*10^7$	<150 µm	
	Considered for	1946–1958				
	rehabilitation					
	Soil					
[5]	Mururoa	Mururoa above-ground: 1966–	6 RP		150–650 µm	Am: 200–500/RP
	IAEA mission	74 (+ safety tests)				
	Soil	Underground: 1976–1996				
[114]	Mururoa	Mururoa above-ground: 1966–	20 RP			Am:
	IAEA mission	74 (+ safety tests)	6 RP		200–600 µm	200–240000/RP
	soil	Underground: 1976–1996				

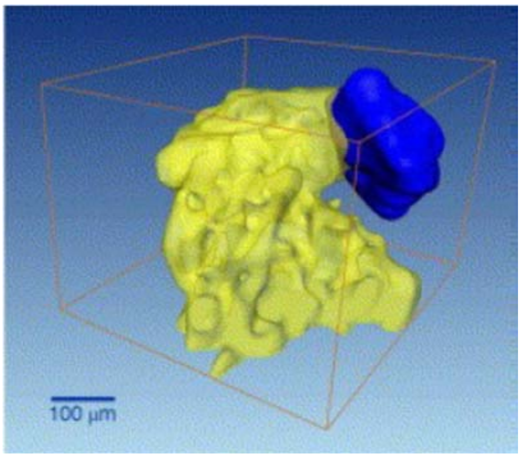


FIG.2. Microtomographic image reconstruction of a Mururoa particle recovered from the surface of the coral atoll according to Eriksson [84]. Distributions of Sr and Pu are represented by yellow and blue colours, respectively.

Semipalatinsk test site, Kazakhstan

A comprehensive study of the radiological situation at the Semipalatinsk test site was performed by the Scientific Production Enterprise 'Aerogeologica' in 1991. A map of ^{137}Cs contamination was prepared. Large fallout fragments (diameters of several mm) were collected from the vicinity of epicentres of the detonations. Fragments had a round (spherical or elliptical) shape and appeared as dark (black or brown) glassy material [115]. Radionuclide compositions were measured and fractionation factors were calculated.

Tests at ground zero resulted in the most wide spread contamination with actinides and fission products, while localized contamination has been attributed to specific nuclear explosions (safety tests). Pu associated with particles or fragments with activity levels exceeding 50 kBq kg^{-1} have been reported by Dubasov et al. [116] and Salbu [3]. Individual tests could be traced by the isotopic ^{240}Pu/^{239}Pu ratio measurements [117].

The Norwegian University of Life Sciences, Norway, and the University of Antwerp, Belgium, have studied a series of radioactive particles isolated from 4 highly contaminated localities using non-destructive microanalytical techniques at the synchrotron facilities at Hasylab and ANKA, Germany [15]. ground zero is the central part of the test site. Lake Balapan (Atomic Lake) was created in the underground explosion of a 140 kt fusion device in 1965. In the Tel'kem 1 and 2 experiments, relatively low yield nuclear devices were detonated resulting in the formation of craters that became filled with water.

Using SEM-EDX, µ-XRF, synchrotron based X ray studies, ICP-MS and AMS measurements, the individual particles were characterized with respect to Pu, U and other metals and correlation between the particle characteristics and the release scenarios was established.

All particles isolated from ground zero were glassy, and vitrified due to the high temperature release scenario [15]. Isolated particles from ground zero contained rather low gamma activities. (<4.5 Bq ^{137}Cs, <0.1 Bq ^{241}Am; Fig. 3). Vitrified material has also been observed at other test sites such as Maralinga and Nevada test sites.

Particles isolated from Tel'kem appeared to be large grains of soil. Within the particles, the presence of highly concentrated small grains (tens of µm in size) was detected. There was a very good linear correlation between U and Pu (at the level of 10–100 ppm) within the particle that may indicate the use of composite fissile cores containing a combination of highly enriched U (HEU) and weapon grade Pu (Fig. 4). Leaching experiments of the separated particles showed different leachabilities of ^{241}Am from the different particles [15].

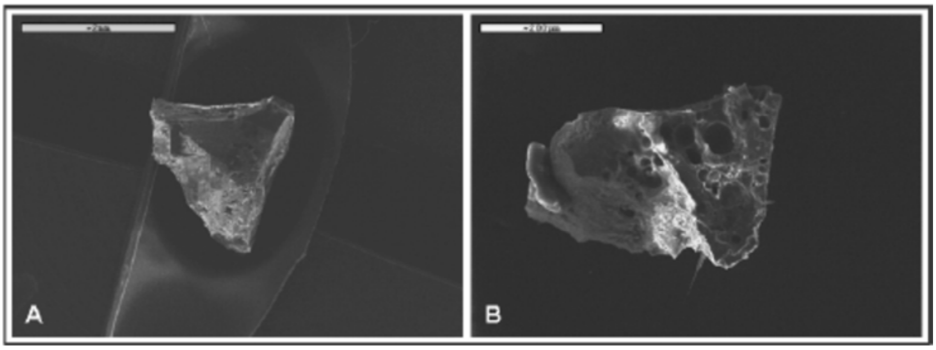


FIG. 3. Electron micrographs of large, vitrified radioactive particles isolated from ground zero, Semipalatinsk NTS. No U or Pu signals were detected using XRMA. The $^{236}U/^{235}U$ *and* $^{240}Pu/^{239}Pu$ *atom ratios of the particle in (B) were determined by AMS (Lind [15]).*

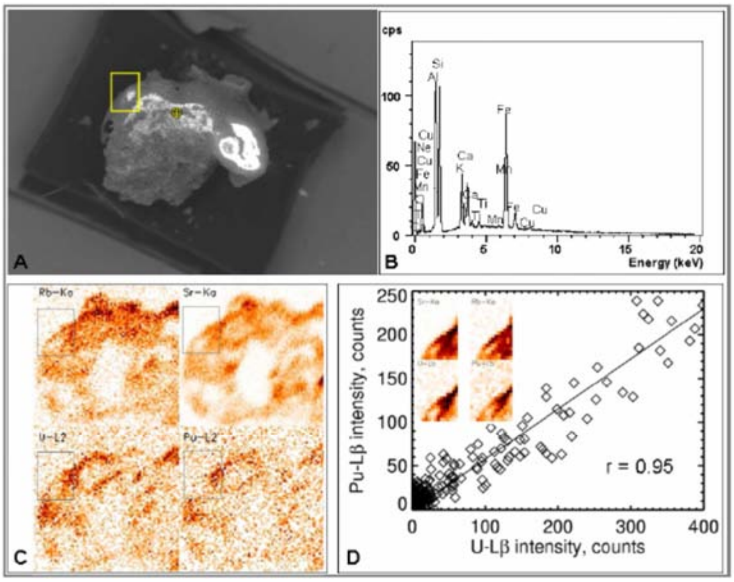


FIG. 4. Radioactive soil particle from the Tel'kem I Crater. (A) Electron micrograph and elemental spot analysis on the indicated spot by XRMA (B). No U or Pu signals were detected on the surface or sub-surface using XRMA. The interior of the particle was further analyzed by means of confocal µ-SRXRF analysis of the particle. (C) Mapping of Rb, Sr, U and Pu in the XZ-plane within the interior of the particle with excitation energy 23.7 keV and live counting time 0.5 seconds per pixel. Dark colours reflect high intensities. (D) U intensities plotted against Pu intensities in individual pixels as determined by mapping of the area within the indicated rectangle. To avoid interferences from Rb and Sr, U Lβ and Pu Lβ intensities were used [15].

Novaya Zemlya, Russian Federation

Significant contamination by actinides and fission products has been localized at 3 major test sites, and contamination of other territories arounhd the test site as well as in southern and north-eastern areas of Novaya Zemlya have been attributed to major events. Sediments have been contaminated (up to 8.5 kBq ^{239,240}Pu/kg) and the total Pu inventory has been estimated at 3 TBq [118].

Detailed microanalytical studies on individual radioactive particles from the test site have not been reported.

In case of other weapons test sites e.g. Reggane, Algeria; Lop Nor, China, detailed information about the contamination and the presence and characteristics of radioactive particles is not available.

4.2. CHARACTERIZATION OF RADIOACTIVE PARTICLES ORIGINATING FROM REACTOR ACCIDENTS

4.2.1. Radioactive particles originating from the Chernobyl accident

The first papers about the detection of radioactive particles of Chernobyl accident origin in European countries appeared already in 1986. Initial observations of Devell et al. were published in Nature in May 1986 [79]. Some radioactive particles were isolated, and gamma spectra showed the presence of Ru and Ba isotopes. The electron microscopic studies revealed the spherical character of the particles with diameters of about 1 μm. The first paper was followed by several others from northern and middle Europe where particles were also found in rain water, air filters, deposits on ground, plants etc. The first information about the analysis of a single radioactive particle found in the region surrounding Chernobyl (in Kiev) was prepared by van der Veen [43] who reported about the gamma and alpha spectrometric and electron microscopic studies of a 30 × 15 μm fuel-like particle.

There are some extensive reviews about radioactive particles of Chernobyl accident origin. The following discussion is prepared based on the papers of Sandalls [119], Pöllanen [50, 120], and Devell [121]. It should be noted that for several years the presence of radioactive particles was referred to as a peculiarity of the Chernobyl accident [12], and the previous particle aspect was reinvented.

Classification of radioactive particles of Chernobyl accident origin based on particle composition

Radioactive particles can be divided into three main groups, as follows.

(A): Monoelemental particles, often called ruthenium (Ru) particles

The name is misleading and originates from the first period following the Chernobyl accident, when the particles were detected by gamma spectrometry and the measured activity derived mainly from ^{103}Ru and ^{106}Ru isotopes. Detailed elemental analysis showed that besides elemental Ru, 'Ru' particles also contained non radioactive elements, mainly transition metals such as Mo, Tc, Rh, Fe, Ni and Pd. Some other radionuclides could also be detected with lower activities e.g. ^{125}Sb, ^{60}Co and some volatile fission nuclides [50]. These particles contained no or little U.

In some cases, radioactive particles were detected from gamma spectra dominated by the ^{140}Ba/^{140}La isotope pair [121, 30]. These particles were referred to as bi-elemental particles. Elemental analysis proved that these particles contain U. Thus, it is more appropriate to list them among the particles belonging to group (B).

(B): Fuel particles

These particles are U oxide fuel fragments containing a range of fission and activation products found in the irradiated fuel, but often depleted in gases and volatile elements. High resolution gamma spectrometry revealed the presence of the following refractory isotopes: ^{239}Np, ^{141}Ce, ^{144}Ce, ^{103}Ru, ^{106}Ru, ^{95}Zr, ^{95}Nb, and ^{99}Mo. Particles were depleted in the volatile isotopes such as ^{131}I, ^{132}Te, ^{137}Cs, ^{134}Cs, sometimes also in Ru and Ba isotopes. High-resolution alpha spectrometry revealed the presence of Pu, Cm and Am nuclides. By means of beta spectrometry, strontium and yttrium isotopes were determined. Minor activities of other radionuclides were occasionally detected (Eu isotopes, ^{125}Sb etc.). The activity ratios of the refractory nuclides (Ce, Zr, Eu, Pu ratios) agreed well with the core inventory of the damaged reactor showing always the Chernobyl accident origin of the radioactive particles. The slightly deviating ratios (^{144}Ce/^{141}Ce and ^{10o}Ru/^{103}Ru) were explained by the variations in the burnup level within the reactor [121, 76, 122]. Elemental analysis of fuel-like radioactive particles often performed by electron probe microanalysis (EPMA) or micro X ray fluorescence (μ-XRF) revealed that U was one of the matrix components often together with zirconium. Other elements detected in the particles were Pb, Fe, Ni, Co, Mo, Zn, Cu, Si, Al, Ca, Cl, and Ti, which can partially originate from the core and from other materials that might have been involved in the fire (see Table 7). Based on μ-tomography and μ-XANES, information on the inner structures and oxidation states of U have been obtained by Salbu and co-workers [83] as illustrated in Section 4.2.1.5.

(C): Condensation particles

A third type of radioactive particles found in the environment was formed by condensation of the volatile elements on secondary particles such as aerosols and soil components. Victorova [123] refers to this group as 'particles of condensation origin' distinguishing the group from other particles belonging to groups (A) and (B) that are listed as a single group in her classification. 'Pure cesium particles' can be mentioned as an example. To emphasize the significance of this group, it has to be mentioned that condensation particles were the major components of the long-range transport and deposition, and were also responsible for the most significant health effect of the accident i.e. the thyroid cancer caused by iodine nuclides.

Of course, all 3 types of particles originate from the fuel of the damaged reactor, and borders among the groups are not always rigid. The present generally accepted classification refers to 3 major groups of particles as listed above. The data bank of radioactive particles of Chernobyl accident origin that was created by experts from Ukraine [124, 125] is based on the same classification.

Another classification was prepared by Dobrovolsky and Lyalko [126]), and Lind [15] that distinguished further types of particles typically found in the vicinity of the plant. Besides fuel-like particles, particles containing construction materials of the damaged reactor were identified e.g. particles with a matrix of nuclear fuel mixed with reactor construction material e.g. (Zr, U)Ox particles and pure construction particles composed of reactor construction materials alone.

Formation of radioactive particles

Group (A):

Sandalls [119] suggested 4 possible mechanisms for the formation of Ru particles, taking into account that they were often spherical:

- Mechanical emission of high temperature liquid droplets from the molten fuel that solidified as they were transported away from the source;
- Liquid droplets formed by homogeneous nucleation of a vapour at a temperature above the melting point of the resulting condensed species: these aerosol droplets could subsequently have solidified into solid particles of similar form;
- Water vapour condensed onto existing water-soluble aerosols to form liquid droplets: the water eventually evaporated from the droplets as they were transported through the atmosphere and away from saturated steam conditions;
- They might have existed within the fuel as 'white inclusions' long before the accident occurred, as has been observed in other fuel.

The major question is whether Ru particles were formed by any of the condensation processes during the explosion or they were already present in the fuel and were dispersed as solid particles as a result of the explosion. The identification of white inclusions containing Ru and Mo by Salbu and co-workers within fuel particles deposited to the west of the reactor [3, 83, 127] justify the latter assumption. Inventory calculations prepared by Pöllanen [50] and estimates by Osuch et al. [128] also support this conclusion.

For melting and evaporation that is followed by condensation, high temperatures are needed. Knowing that the melting point of Ru is 2310^{o}C, Devell [121] suggested that this had to be exceeded to get liquid droplets. This was considered unlikely according to Russian experts[1]. However, volatile oxides of Ru may form at much lower temperatures provided sufficient amount of oxygen is present. Such

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[1] Personal communication with S. Gordeyev and E. Kvasnikova.

conditions could have occurred if small particles were dispersed into the atmosphere as a result of the explosion. The volatile oxides formed in the atmosphere could later be reduced to the metal form e.g. by the burning graphite. Finally Ru could condense on the surfaces of aerosols or fuel-like particles. This would explain the formation of Group B particles which have varying depletion of Ru.

Ru particles may have existed as metallic precipitates in the fuel elements before the accident. According to the investigations on irradiated UO_2 samples it was possible to observe 'white inclusions' up to 5 μm in size, on the UO_2 grain boundaries, consisting of Mo-Ru or Mo, Tc, Ru, Rh, or Pd. In the course of irradiation the precipitates could grow to 20 μm in size. It was also shown that the precipitates occurred in two phases. The contents of Mo and Ru are complementary, those of Tc, Rh and Pd are more or less constant in both phases. This is supported by the results from synchrotron radiation microanalysis of particles released during the initial explosion reported by Salbu et al. [83], and supported by Kashparov [129], proposing that spherical Ru particles detected in Western Europe could have been present in the nuclear fuel at the moment of the accident, whereas large and irregularly shaped Ru particles deposited near the plant were formed at the rate of Ru oxidation during the accident and its subsequent condensation on the particles of materials of iron group elements.

Schubert [81] compared the Ru radioactive particle composition determined by elemental analytical techniques and the particle size with the same properties of the metallic precipitates:

- The fission product elements Mo, Tc, Ru, Rh, Pd as well as Fe and Ni were contained in the radioactive particles and in the metallic precipitates in irradiated fuel elements. The ratios of the elements in radioactive particles varied to a great extent, similar to those in precipitates in fuel. Both materials were essentially free of oxygen;
- The size of the radioactive particles was in the same range as that of the metallic precipitates in fuel (4–14 μm).

In accordance with results from Salbu and co-workers, Schubert concluded that Ru particles were formed in the fuels before the explosion. The theory of white inclusions may not, however, explain the presence of some other radionuclides found in the Ru particles e.g. ^{60}Co as suggested by Broda [122].

Group (B):

It is likely that the irregular shaped fuel-like radioactive particles were formed by mechanical disintegration of the fuel in the explosions. The more spherical particles were probably produced in situ in the burning fuel. The depletion in some volatile elements may have been the result of evaporation since the fuel temperature is likely to have exceeded 2000°C.

Oxidation state of U in fuel-like particles:

The oxidation states of U in the particles found in the close vicinity of the damaged reactor have been determined using the synchrotron radiation based XANES technique by Salbu and co-workers [3, 15, 83, 127]. Particles released during the fire and deposited to the north showed a UO_2 core covered by a layer of oxidized U i.e., U_2O_5/U_3O_8, while particles released during the explosion and deposited to the west had a UO_2 core covered by a layer of apparently reduced U (oxidation states between metallic U and UO_2) associated with carbide or Zr. Since fuel elements are made of high density UO_2 pellets, it is evident that some U was oxidized in the reactor fire, while other part remained unchanged or was partially reduced certainly due to the interaction with graphite.

Particles resulting from two different high temperature scenarios were released into the environment. During the initial explosion on April 26th, mechanical destruction of the UO_2 fuel occurred at high temperature and under high pressure, in the presence of the graphite moderator. During this period, deposition of fuel particles took place to the west of the reactor. During 26–30 April, volatile fission products and U fuel particles were released under high temperature and oxidizing atmosphere due to the fire and deposition of the particles occurred to the north, northeast and south of the plant. From April 30th to May 6th, the temperature was lowered and subsequently the emission of volatile elements decreased [54, 83, 127, 129].

Uranium in the initial explosion was partially reduced, thus fuel-like particles west of the plant contained apparently reduced U (U-O-Zr, carbides). Uranium in the particles released after the initial explosion was oxidized, thus fuel-like particles in the north, northeast and south of the reactor have higher oxidation states. Reduced U has low solubility and low weathering constant (inert towards leaching), while oxidized U has higher solubility and increased weathering constant (sensitive to leaching).

By these pioneering works it was shown that, although the source was the same, changes in the release scenario affected particle characteristics (oxidation state and morphology), and had an essential long-term effect on mobility, weathering and soil-to-plant transfer of radionuclides associated with the particles. It was also predicted that radionuclides will be leached faster from the oxidized particles in the north, northeast and south regions than from the reduced species in the west region of the plant.

Beside the conventional contamination maps showing the spatial distribution of ^{137}Cs, maps of ^{90}Sr and Pu distribution have been prepared and a map of the leachability of the radionuclides (soil-to-plant transfer factors) has also been constructed for the exclusion zone in Ukraine [54, 124, 129]. See also recommendations on measurement of individual particles in section 4.7.6.

Particle size and particle activity

Particle sizes (d_p) were usually measured by different techniques. Electron microscopes or sometimes optical microscopes, autoradiography and nuclear track detectors are applicable for the determination of particle sizes. Knowing the shape factor and density of a particle, its aerodynamic diameter (d_a) can be calculated. In case of a spherical UO_2 particle where the density is 10.5 kg dm^{-3}, $d_a \approx 3.2 \cdot d_p$.

Particle size can roughly be estimated from total activity or nuclide specific activities using reactor core inventory data. Size estimation is based on the assumption that radioactivity (ratios) of the nuclides involved in calculations is not changed during fuel fractionation processes, which probably is not correct. The equivalent volume diameter d_p (µm) is calculated from the known activity per unit volume A_{vol} (Bq μm^{-3}), of a nuclide or a sum of nuclides

$$d_p = \left(\frac{6A_{meas}}{\pi A_{vol}} \right)^{1/3}$$

where A_{meas} is the measured activity of a nuclide or sum of nuclides in Bq.

Size was estimated separately for Ru and U fuel particles. According to Pöllanen [120], the following activity per unit volume values were suggested for the Ru and U particles:

$A_{vol\text{-}Ru} = 100\ Bq\ \mu m^{-3}$

where $A_{vol\text{-}Ru}$ refers to the measured activity of $^{103}Ru+^{106}Ru$.

$A_{vol\text{-}U} = 0.7\ Bq\ \mu m^{-3}$

where $A_{vol\text{-}U}$ refers to the measured activity of $^{95}Zr+^{141}Ce+^{144}Ce$.

This method gives a rough estimate of the particle sizes. In Table 8, d_a values were measured or calculated according to the above equations.

A summary of the particle sizes and activities is given in Table 8 according to Pöllanen [120]. In Table 8, only those studies are mentioned in which either single particles were detected and further analyzed or particle sites were directly measured and detailed properties of the particles were given. The number of analyzed particles, their activites and aerodynamic diameters are given for both uranium fuel particles (U) and ruthenium particles (Ru). Particles were categorized as U and Ru type particles. Only the total number of analyzed particles is given. Particle sizes (‘physical’ diameter) given in the references (microscopes or other means) are preferred (conversion into aerodynamic diameter is performed here) and are denoted as asterisk.

TABLE 8. RADIOACTIVE PARTICLES ORIGINATING FROM THE CHERNOBYL ACCIDENT AND DETECTED IN EUROPE. Adapted from [120]

First author	Sampling site	No. particles		Activity (Bq)		Aerodyn. diameter (μ)	
		U	Ru	U	Ru	U	Ru
Rytömas [130]	Uusikaupunki	8	1	120	200	23	5. 2
	Soviet train carriage	4	1	15000	29000	110	
Mattson [131] a)	Helsinki			$>200^{tot}$		>16	
	Nurmijarvi			$>200^{tot}$		>16	
Sinkko [132]	Nurmijarvi	8	2	$18^{\text{Ce-144}}$	$9^{\text{Ru-106}}$	18	3.3
Kauppinen [133] b)	Helsinki					>16	4.4
Saari [41] c)	Uusikaupunki	20	1	320	130	15	
	Lohja	1		45		8	
Paatero [134]	Helsinki	1		140		24	
	Nurmijarvi	1					
Devell [121]	Nyköping	6	6	750	31000	41	27
Kerekes [135] c)	Stockholm	9	9	$110^{\text{Ce-144}}$	49000	33	37
	Gotland	5	5	$67^{\text{Ce-144}}$	5300	28	15
	Gavle		13		9800		7.8
Robertson [134]	Gavle	1		380		33	
Perkins [137] c)	Alvkarleby	2		450		35	
	Stockholm	3	1	380	7400	33	17
	Nyköping	6		420		34	
	Gusum	7		250		29	
	Vastervik	9	1	340	9300	32	18
	Oskarshamn	4		440		34	
	Öland	2	1	160		24	
Salbu [138]	Kjeller		1		$65^{\text{Ru-106}}$		6.3
Lujanas [139] d)	Vilnius					22d	
Schubert [81]	Masuria Lakes	1	8		170000		45
Osuch [128] a)	Mikolajki	9	51	4000^{tot}	200000	44	51
	Warsaw	10	11				
	Lomza	12	7				
	Bialystok	82	12				
	Suwalki	1	7				
Broda [140, 76, 122] a)	Mikolajki and Krakow	28	37	2000^{tot}	308000	35	58
Van der Wijk [45]	Poland	1	3	36	90000	15	39
	Kiev	1		950		45	
	Minsk	1		420		34	
Georgi [141] b)	Neuherberg, Vienna					<16	
	Helgoland, Hannover						
Kolb [142]	Brunswick	12^{tot}		15^{tot}		6.9	
Reineking [143]	Göttingen	3		3.1		5	
Wahk [144]	Konstanz	10	5	41	270	16	5.6
Behrens [145]	Neuherberg	1	3		3100		13
Winkelmann [146] b)	Neuherberg					<10	
Horn [147] b	Aachen					<10	
Burkart [148]	Würelingen	1	1	40	360	15	6.2
	Baar	3	2	35	79 $3000^{\text{Ru-103}}$	15	4
Jost [149] b)	Spiez, Zürich					<7	
Rulik [150] b)	Krumlov, Ostrava, Prague					<7	
Keck [151]	Vienna	2		66		18	
Balashazy [31]	Budapest	12	3	230	570	33	72
Lancsarics [152]							
Dovlete [153]	Iaci	3		$59^{\text{Ce-144}}$		33	
	Tulcea	1		$57^{\text{Ce-144}}$		26	
	Craiova	1		$110^{\text{Ce-144}}$		27	
Mandjoukov [28]	Sofia	5				4-20	

TABLE 8. RADIOACTIVE PARTICLES ORIGINATING FROM THE CHERNOBYL ACCIDENT AND DETECTED IN EUROPE. Adapted from [120] (cont.)

First author	Sampling site	No. particles		Activity (Bq)		Aerodyn. diameter (μ)	
		U	Ru	U	Ru	U	Ru
Kritidis [154] a)	Athens, Thessaloniki	18	6	240	43000	28	30
Misaelidis [155]	Thessaloniki		1		1500		9.8
Cuddihy [156]	Shipping crate	10^{tot}				<50	
Pavlotskaya [157]	30 km zone	7^{tot}		$16000^{\mathrm{Ce-144}}$		170	
Tcherkezian [158]	30 km zone	10^{tot}		$9900^{\mathrm{Ce-144}}$		150	
Salbu [11]	30 km zone	10^{tot}		$950000^{\mathrm{Ce-144}}$		680	
Khitrov [159]	Vil'cha	1^{tot}		$16000^{\mathrm{Ce-144}}$		170	
	Kiev	1^{tot}		$660000^{\mathrm{Ce-144}}$		140	
Lyul [160]	Near plant	10^{tot}		$40000^{\mathrm{Ce-144}}$		240	
Rudhard [161]	Near plant					100	
Kutkov [162]	Plant staff					12 (AMAD)	
Demchuk [163]	Near plant					45 (mean)	
IAEA [164]	Polesskoe	1^{tot}		$70^{\mathrm{Ce-144}}$		28	
Burakov [165]	<12 km from plant	1^{tot}				>200	
Akopova [57] d)	30 km zone	56^{tot}				<200d	
Kuriny [166] e)	<10 km from plant	1200^{tot}				20–400e	
Krivokhatsky [167]	0.5–12 km from plant					>1 mm	
Vapirev [30]	Sofia	1		100		5	
Vapirev [29]	Sofia	1		2300		1–15	
Pöllanen [32]	Baltic Sewa	1				10	
Hohenemser [168]	Konstanz		1				1–2
Kashparov [129]	Near plant	500				1–10, 50–80, 500–700	
Papp [169]	Kiev	59					
Raunemaa [80]	Uusikaupunki	20	1	90–560			
Falk [27]	Stockholm, Gavle, Gotland	13	23	80–350	300–40000	<12	
Knizhnik [60]	Kiev						
Kashparov [54]	Chernobyl (<30 km)						

a) Detailed activity data of individual particles are given for only a few particles or not at all.

b) Impactor measurement; aerodynamic diameter (maximum size) of particles are given as such.

c) Particle sizes (SEM) do not necessarily match calculated sizes.

d) Particle size is determined using emulsion techniques (dp is presented).

e) Chernobyl radioactive particles data base was created consisting γ- spectrometric data of 1200 particles with characteristic sizes 20–40 mm (not d_a) and activities more than 37 Bq (1987).

If the particle sizes are not given in the original study, aerodynamic diameters are calculated using methods given above. The activity of U particles refers to the sum of activities of ^{95}Zr, ^{141}Ce and ^{144}Ce. The activity of Ru particles is the sum of ^{103}Ru and ^{106}Ru. Sometimes the references give only the total activity of the particles or the activities of the long-lived nuclides ^{106}Ru and ^{144}Ce.

The aerodynamic sizes of radioactive particles found in different locations in Europe varied from some μm to the range of mm, depending on the distance from the Chernobyl NPP and the type of radioactive particle, Ru particles being typically smaller than U ones. Activities of the single radioactive particles varied also in a wide range from some Bq in the case of particles detected in Western Europe to MBq for those found in the direct surrounding of the reactor. Higher specific activities were measured in Ru type radioactive particles.

Fractionation

In the case of nuclear tests, primary fractionation took place during nuclide and particle formation in the fireball, followed by secondary fractionation. In the case of the Chernobyl accident, however, an a priori fractionation occurred in the fuel elements before the accident as a result of inhomogeneities in burn up processes in the reactor core.

Inventory calculations were performed for the RBMK reactor of the Chernobyl NPP by Piasecki et al. [170] as a function of known and supposed operation conditions, including power history and exposure times of the fuel elements. The RBMK reactors usually work in a continuous reloading regime. During the time of the accident on 26th April 1986, the reactor overwhelmingly comprised (75%) first-load rods that had been loaded at the start up in December 1983 and additional younger ones. Most probable activity ratio values for the isotope pairs i.e. ^{106}Ru/^{103}Ru, ^{144}Ce/^{141}Ce, ^{134}Cs/^{137}Cs were calculated and compared with ratios determined experimentally in radioactive particles found in the environment in Poland. On the basis of these calculations the measured fuel-like radioactive particles (B type) were classified into two further groups: those originating from the first load and those from younger fuel rods. A procedure for relative dating of the younger radioactive particles has been proposed. The investigations did not reveal significant initial Pu enrichment of the fuel elements.Further fractionation processes in fuel-like radioactive particles from the fallout have been analyzed by Jaracz et al. [171]. Distribution of the above mentioned activity ratios, correlation coefficients between different activity ratios as well as those of fractionation factors were determined, and analyzed by statistical methods. Processes which can be responsible for fractionation of certain fission products in radioactive particles include: evaporation of volatile elements (Cs and Ru) relative to refractory ones, thermal diffusion within fuel rods (responsible for anomalies in Ce ratios) and 'half-life effects' influencing the spatial dependence of isotope ratios of the same elements (e.g. Ce and Ru). The analyses proved the absence of significant mixing between non-volatile fission products from different parts of the core.

Analysis of individual radioactive particles sampled in the exclusion zone around the Chernobyl NPP

Synchrotron radiation based micro and radioanalytical techniques have been developed for the characterization of individual radioactive U particles originating from the exclusion zone of the Chernobyl NPP using the ESRF facility in Grenoble, France. Salbu et al. [10, 12, 15, 83] studied fuel-like particles from regions west and north of the plant using SEM-XRMA and SR based μ-X ray techniques to obtain information on elemental composition and distribution, porosity, crystallographic structures and oxidation states of U. Particles were separated from soil and dust samples.

Using scanning electron microscopy (SEM), large particles, spherical grains or small crystallites varying in size from a few to several hundred microns could be identified. XRMA spot measurements confirmed the presence of U and Zr in the particle sampled in the west part of the Chernobyl exlusion zone, while only U was observed in the particle from the north. μ-XRF screening of particles demonstrated that Sr, Ru and Mo were also present as white inclusions in particles from the western region. SEM image, μ-tomographic reconstruction and computerized slicing of the 3D image of a UO_2 particle collected from the west of the reactor are shown in Figure 5. This is the first tomographic reconstruction of any micrometre sized U fuel objects.

μ-XANES measurements demonstrated that fuel particles released during the initial explosion were not oxidized and some particles contained apparently inert, reduced forms of U associated with Zr or carbide. The μ-XRD results confirmed the conclusions.

The tomographic reconstruction of a fuel particle containing oxidized U released during the fire is depicted in Figure 6. The image reflects a heterogeneous structure which is very different from the crystalline structure shown in Figure 5 for fuel particles released during the initial explosion.

Results from the μ-XANES imaging demonstrated that a particle released during the reactor fire (north of the reactor) was characterized by a UO_2 core surrounded by oxidized U (U_2O_5/U_3O_8 layer). μ-XRD confirmed the conclusion that U in the UO_2 fuel particles released during the reactor fire was oxidized to U_3O_8 and possibly other intermediate forms.

The great variety of the radioactive particles collected in the 30 km exclusion zone of the Chernobyl NPP is represented by the 'hot particle' data bank that comprises information about 2000 particles including SEM images [125].

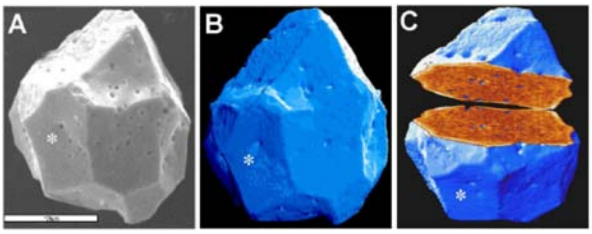

*FIG. 5. μ-tomography of a U fuel particle from Chernobyl containing reduced U according to Salbu et al. [83] and Lind [15]. (a) Scanning electron microscopy image of the fuel particle containing non-oxidized U. Bar 20 μm. (b) 3-D rendering of 500 tomographic slices of the particle in (a) taken by rotating the sample 180° using 17 keV X ray. Each projection image consisted of 1024 × 1024 pixels. (c) 3-D visualisation of the particle in (a). By computirize slicing the inner structure of the particle is revealed. The * in figures a, b, and c indicates the same position at the particle surface.*

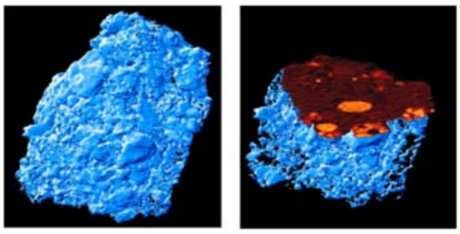

FIG. 6. μ-XAS-tomography of an oxidized fuel particle released during the fire in the Chernobyl reactor according to Salbu et al. [83] and Lind [15]. (Left) 3-D rendering of tomographic slices showing the surface of the particle. (Right) Computerized slicing of the 3-D image of the oxidized fuel particle.

Analysis of individual radioactive particles of Chernobyl accident origin collected in Europe

Radioactive particles originating from the Chernobyl accident were collected at many places in Europe (see the previous section) and a few of them were individually characterized. A few examples are shown below.

Following April 28, 1986, rain water in Oslo contained radioactive particles [172]. A Ru particle was also found in Norway by Salbu et al. in 1987 [138]. The SEM image of the particle is shown in Figure 7.

A fuel-like radioactive particle originating from the Chernobyl accident was collected in 1995 in a marine sediment sample from the Baltic Sea by Pöllanen [32] and subjected to detailed radiochemical (gamma, beta and alpha spectrometric) and microanalytical (SEM-EDX) studies. An SEM image of the particle is depicted in Figure 8.

According to SEM-EDX measurements the particle contained mainly U (40–50%), Zr (30–40%) and minor amounts of Al, Si and Fe. The particle had probably been in a molten state, because U and Zr were evenly distributed and no granular structure was observed. Elemental composition, nuclide composition and structure of the particle suggested that the particle originated from the Chernobyl accident.

4.2.2. Radioactive particles originating from other reactor accidents

The Windscale reactor accident

The Windscale reactor was a gas-cooled, graphite moderated reactor using metal U as fuel, and was basically different from the RBMK type reactors that had been operated at the Chernobyl NPP. The scenario of the events resulting in releases of actinides to the environment was also different from that of the damaged Chernobyl unit.

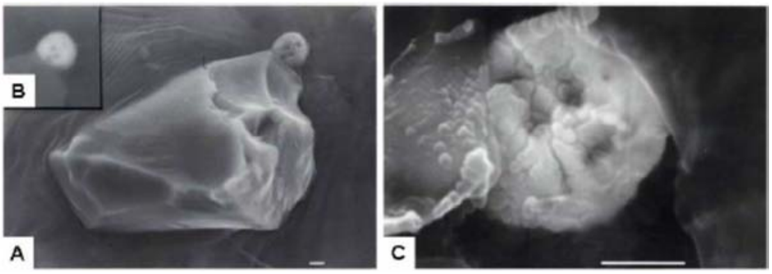

FIG. 7. Scanning electron micrograph of a Ruthenium particle found in 1987 in Valdres, Norway by *Salbu and co-workers [138] A) Overview of the Ru particle attached to a larger silicon particle, SEI-mode; B) Close up of the Ru particle, BEI-mode. Bright areas show the presence of elements with high atomic numbers; C) Higher magnification of the radioactive particle, BEI-mode.*

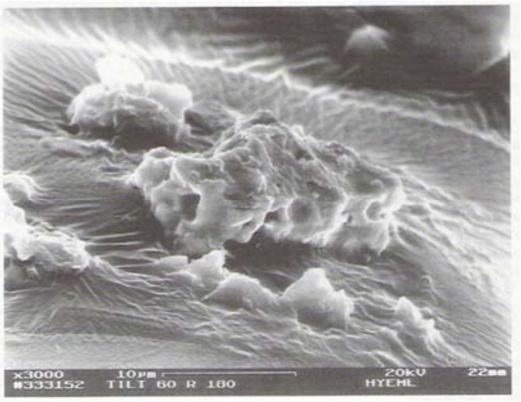

FIG. 8. Secondary electron image of a particle originating from the Chernobyl accident and collected from Baltic Sea sediment [32]. The irregularly shaped particle located in the middle is surrounded by inactive sediment particles.

Due to low temperature corrosion of spent fuel elements and the lack of an efficient air filter system, fuel particles containing actinides and fission products were released into the atmosphere from about 1952 to 1957. Contaminated soil collected in 1956 in Seascale, in the vicinity of the Windscale Nuclear Installation, was stored until 1992 when it was subjected to particle separation and analysis by Salbu [10]. Particles that were analyzed must have originated from the 5 year-long lasting pre-fire releases. Based on electron microscopy, the particles had a flake-like structure, significantly different from those observed in the Chernobyl fallout [11]. The particles were inert towards leaching with 1 M HCl [173]. A scanning electron microscopic image of the particle is shown in Figure 9.

After a graphite fire that broke out in Pile 1 in 1957, the reactors were shut down. Due to the graphite fire, ^{239}Pu was released, probably associated with U oxide. Particles in the size range of 20–500 µm were observed up to 4 km from the site [16, 174]. Many large particles up to 700 µm in length [16] were emitted through the stack.

The Sosnovyy Bor reactor incident

A limited number of investigations have been carried out to characterize radioactive particles originating from other reactor accidents, most probably due to the lack of relevant techniques. One interesting example is the study performed by Toivonen et al. [175] to separate and identify a radioactive particle from an air filter sample collected in Finland. Radiochemical studies proved that the particle originated from the accident of the Sosnovyy Bor NPP near Leningrad, Soviet Union, in 1992.

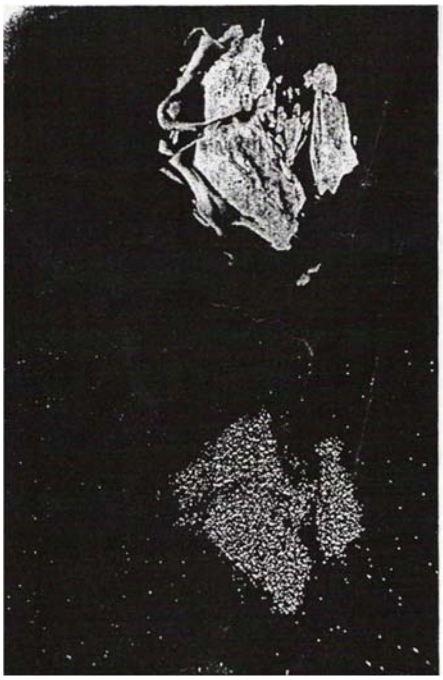

FIG. 9. SEM image of a particle originating from the Windscale reactor accident [11]. Upper part, SEM image in BEI mode; lower part, X ray mapping of uranium.

4.3. RADIOACTIVE PARTICLES ORIGINATING FROM INADVERTENT DESTRUCTION OF NUCLEAR WEAPONS

Similar sources and similar release scenarios characterize the radioactive particles that originate from the B-52 bomber accidents at Palomares, Spain in 1966 and at Thule, Greenland in 1968. In both accidents the bombers crashed and caught fire. The U and Pu containing material of the thermonuclear bombs detonated conventionally. The explosion and the subsequent fire caused the dispersion of the material in the environment, on land in case of Palomares and on ice and sediments as well as on soil in case of Thule.

Individual radioactive particles were collected and separated from soil and sediment many years after the accidents to characterize the particles by applying up-to-date analytical techniques and to study the long-term environmental behaviour.

Eriksson and co-workers [84] studied 6 radioactive particles originating from the Thule accident that were collected in the missions in 1968, 1979 and 1997. The work was also summarized in the review paper on environmental radioactive particles [176]. The particles were investigated by gamma-ray and X ray spectrometries, SEM coupled with EDX and WDX spectrometers, synchrotron radiation based μ-XRF and μ-tomography (Fig. 10). It was concluded that U and Pu were mixed in the particles. The U/Pu mass ratios varied between 0.05 and 0.36. The SEM image of one Thule particle with corresponding EDX-spectrum and the U and Pu intensity maps obtained by μ-XRF are shown in Figure 10.

The results of μ-tomography showed that that U and Pu were not homogenously distributed within the particles. Figure 11 shows an example of the 3D distribution of U, Pu and the matrix element Fe in the reconstructed image of one Thule particle.

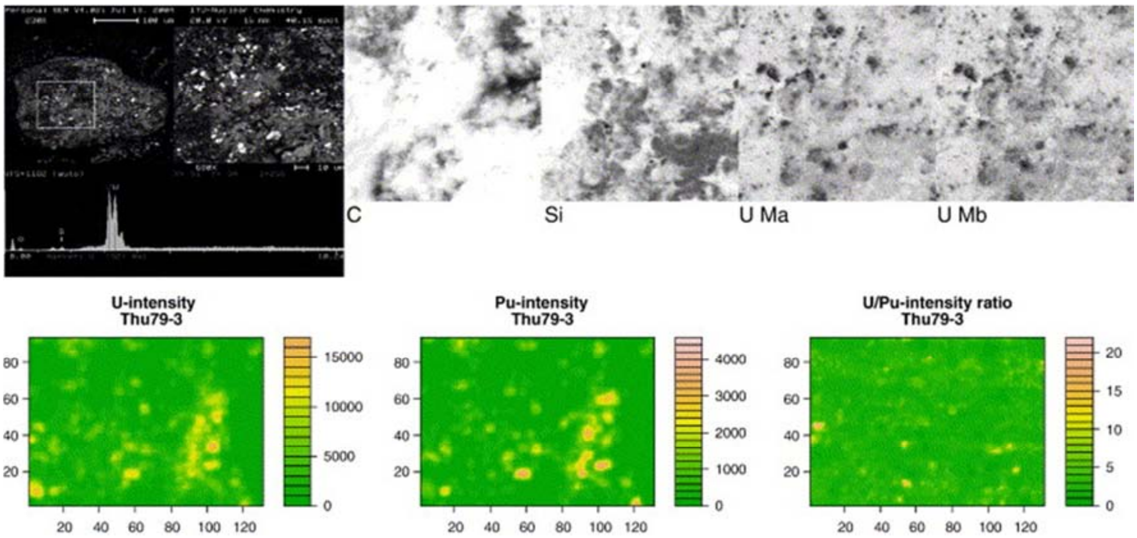

FIG. 10. Upper row, Backscattered electron image of a particle originating from the Thule accident and elemental maps determined by µ-XRF (100 × 130 µm2). Bottom row, U and Pu L-line intensity maps, the unit of the colour scale is cps, the unit of the x-y scale is µm; according to Eriksson [84].

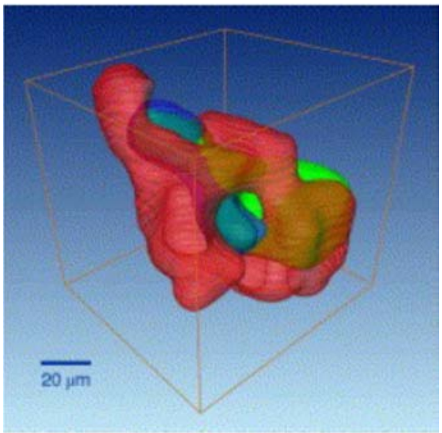

FIG. 11. µ-tomographic reconstruction of the distribution of elements in a U/Pu rich particle recovered from the sea sediment after the Thule accident [84, 176]. The Pu (blue) and U (green) are coated with iron (red) rich sediment matrix.

The Thule particle recovered from sea sediment after a long residence time had been partially coated with a Fe-rich sediment matrix. The oxidation states of U and Pu in the particles were determined by µ-XANES. It was shown that U(IV) was the preponderant species. As relates to Pu two types of particles were identified. According to Eriksson et al. [84], one set had about 90% Pu(IV), while in other ones the ratio of Pu(IV) to Pu(VI) was about one to three. From the results it was expected that the mobility of the particles in the environment would be different. The ^{241}Am/$^{238+239+240}$Pu activity ratios varied between 0.13 and 0.17, indicating that the particles originated from different source terms. Eriksson also reported ^{235}U/^{239}Pu and ^{235}U/$^{235+238}$U mass ratios for the Thule particles in the range of 1.14–3.90 and 0.454–0.534, respectively.

Pöllanen [21] studied one radioactive particle separated from a soil sample that was taken in Palomares in 1998. Isolation of the particle was performed using gamma spectrometry and imaging plates. SEM and X ray microanalysis revealed the presence of U and Pu as well as Pb and Fe. The spatial distributions of Pb and Fe were different from those of U and Pu. Particle diameter was about 10 µm. Radioisotopes of U, Pu and Am were analyzed using non-destructive and destructive radiometric methods, ICP-MS and SIMS. The elevated ^{235}U/^{238}U atom ratio (1.55) indicated the presence of enriched U, and the Pu atom ratios (^{240}Pu/^{239}Pu: 0.068 and ^{241}Pu/^{239}Pu: 0.0093) were consistent with weapons-grade material. Comparing the the mass ratios of U, Pu and Am isotopes, Pöllanen concluded that the radionuclide composition of the Palomares particle was not very different from the Thule particles analyzed by Eriksson.

Using ESEM and synchrotron radiation microtechniques, Lind et al. [89] studied 5 particles that were collected from soil in Palomares in 2001 and 3 particles from sediment in Thule in 1997. Characteristics of the particles originating from the two accident sites were similar in several ways:

- The size of the isolated particles ranged from about 1 to 50 µm;
- U and Pu coexist throughout the particles;
- Variations in the Pu/U element ratio between particles from each site, as well as between Thule and Palomares particles were observed;
- Average Pu-Lα/U-Lα ratios were 2–3 times higher for Palomares particles than for Thule particles;
- Surface inhomogeneities on both Palomares and Thule particles were observed;
- The particle matrices are U and Pu oxide mixtures, most probably in form of mixed oxides/oxyhydroxides;
- The oxidation state of U seems to be predominately +IV (UO_2) with a minor and variable contribution of higher oxidation states (U_3O_8), and Pu seems to be present as Pu(III)/Pu(IV), Pu(IV)/Pu(V) or a mixture of all three oxidation states;
- The ^{240}Pu/^{239}Pu atom ratios of the Palomares and Thule particles were 0.061±0.006 and 0.055±0.007, respectively;
- ^{235}U was the major fissile material in both a Palomares and a Thule particle with ^{239}Pu/^{235}U atom ratios of 0.78±0.14 and 0.62±0.13, respectively;
- ^{241}Am/$^{239+240}$Pu activity ratio was 0.19±0.02 for the Palomares particle and 0.14±0.02 for the Thule particle.

As examples, SEM images and XRF spectra of a Palomares and a Thule particle are shown in Figures 12 and 13 [15, 89]. Based on the microanalytical results the following conclusions were drawn about the accident and the environmental consequences:

- The original metallic U and Pu in the bomb was oxidized in the explosive fires;
- The weapons involved in the Palomares and Thule accidents were based on composite material fissile cores where ^{235}U was the major component;
- The Palomares and Thule particles have persisted in the terrestrial and marine environment for three decades. They are highly inert under the conditions that have prevailed, although increasing solubility is expected in the future;
- The source origin was verified by the isotope ratio measurements.

4.4. DEPLETED URANIUM PARTICLES

Depleted uranium (DU) ammunitions were used during the Gulf war in Kuwait and the Balkan incidents in Bosnia-Herzegovina and Kosovo. Individual radioactive particles originating from these sites were studied by several research teams, and Betti et al. [176] prepared a short review about the results of the investigations.

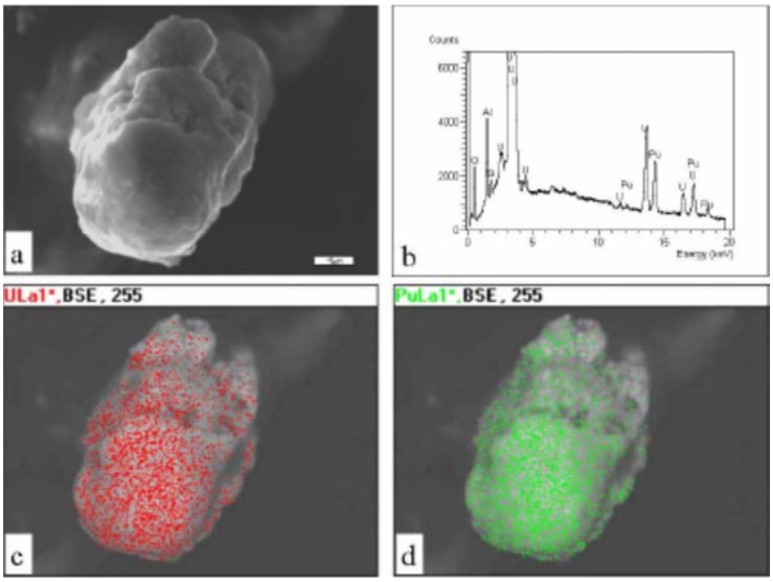

FIG. 12. Scanning electron microscopy of particle B isolated from soils collected at Palomares, Spain: (a) secondary electron imaging (SEI) mode reflecting the morphological structure of the particle, (b) elemental spot analysis by XRMA, (c) and (d) X ray mapping of U and Pu superimposed on a BEI mode image. Bar 5 µm [15].

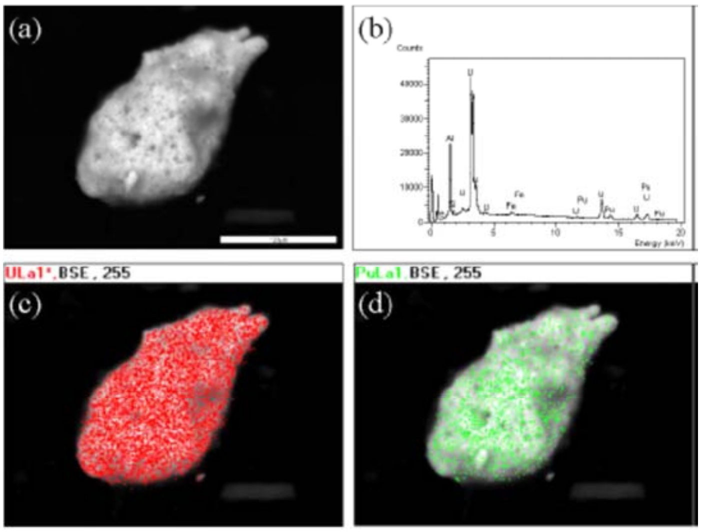

FIG. 13. Scanning electron microscopy of particle #133 isolated from sediments collected at Bylot Sound, Greenland (Paper IV): (a) Secondary Electron Imaging (SEI) mode image reflecting the morphological structure of the particle, (b) elemental spot analysis by XRMA, (c) and (d) X ray mapping of U and Pu superimposed on a BEI mode image. Bar = 20 µm [15].

DU particles collected in soil samples have been studied by Danesi et al. [24, 96], Salbu et al. [25, 177, 178] and Török et al. [179, 180].

Soil samples collected from Kosovo some years after the war contained fine particles with DU as the major component, and investigation of the particle distribution showed that most particles were small [28, 29]. Fine DU particles of µm size were often attached to bigger soil particles that contained Ti and Al as typical components of the penetrators and their claddings.

U isotope compositions determined AMS [24, 177, 96] and by SIMS [180] clearly revealed the depletion of U (mass ratio of $^{235}U/^{238}U$ was about 2E-3) and the presence of ^{236}U (wt% of 0.003–0.01) indicating that reprocessed U was used for DU production. Török et al. [180] also investigated the oxidation state of U in DU particles by µ-XANES and showed that U is present in the particles mainly as U(IV), the maximum ratio of U(VI) to total U content was 24%.

Salbu et al. [25, 178] and Lind [15] analyzed DU particles originating from Kosovo and from 3 different sites in Kuwait using SEM-EDX combined with different synchrotron radiation micrpotechniques. Small-sized (sub-micron to 30 µm) DU particles were collected in soil from underneath jacket in Kosovo. Small particles were also obtained close to impacted DU penetrators, corroded 'unspent' DU penetrators in Kuwait, whereas large DU particles (up to several hundred µm) were released during the fire in a DU ammunition facility at Al Doha, Kuwait. DU particles from all investigated samples were identified directly by SEM and XRMA (Figs. 14–15).

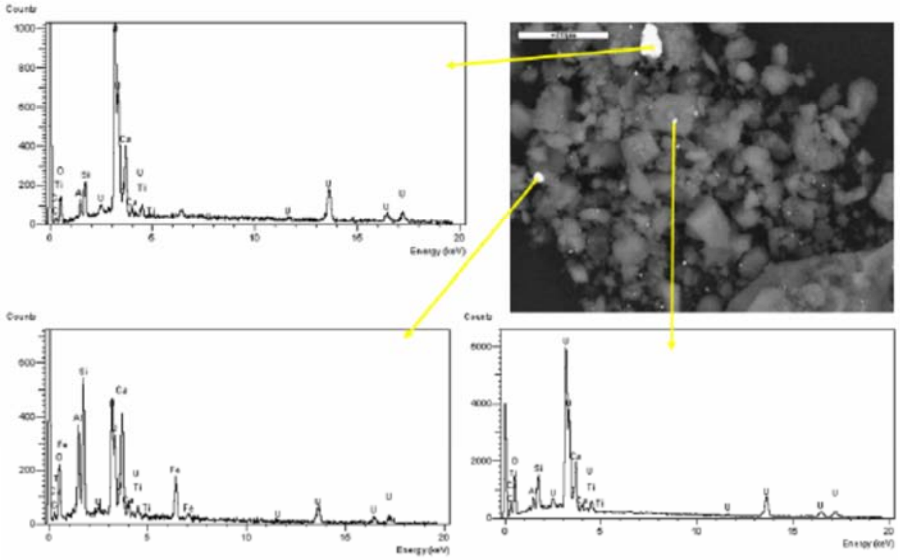

FIG. 14. Scanning electron microscopy of DU-particle contaminated soil collected at Ceja Mountain, Kosovo. Backscattered Electron Imaging (BEI) with bright areas reflecting high atomic number elements are clearly visible. XRMA spectra from spot measurements on bright areas (yellow arrows) confirm the presence of U and Ti. Bar = 20 µm. [15].

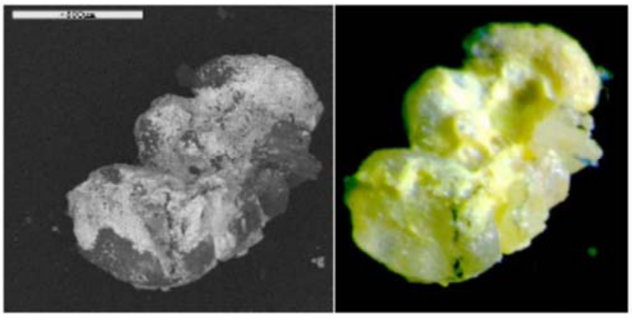

FIG. 15. Grain of sand partly covered with depleted U originating from the ammunition storage fire in Al Doha, Kuwait. (left) Scanning electron micrograph recorded in BEI mode. (right) Light microscopy image of the same particle [15].

Oxidation states of U were determined by µ-XANES, and confirmed by µ-XRD. Characteristics of DU particles in soil and/sand from Kosovo and Kuwait, respectively, varied significantly depending on the release scenario [25, 177]:

- Bright yellow, highly oxidized DU (U_2O_5/U_3O_8 and U(VI)) particles with a wide size distribution from submicron to several hundred micrometre were associated with the fire in an ammunition storage facility. DU in sand samples contaminated with these particles had high solubility in simulated gastrointestinal fluid;
- In contrast, the initial extraction of soil and sand samples contaminated with smaller and less oxidized DU (UO_2, U_3O_8 or a mixture of these oxidized forms) particles, originating from the corrosion of DU penetrators or collected in tanks hit by DU ammunition, appeared to be less soluble;

- The presence of respiratory U particles with oxidized forms higher than UO_2 was also revealed.

Atom ratios ($^{236}U/^{235}U$) obtained from ICP-MS and AMS demonstrated that U in the DU-particles in Kosovo as well as in Kuwait originated from reprocessed fuel.

4.5. RADIOACTIVE PARTICLES RELEASED FROM REPROCESSING PLANTS

4.5.1. Mayak

Radioactive particles originating from the Mayak reprocessing plant were collected from sediments of the water reservoirs and from soil along the Techa River and studied by various microanalytical techniques by Salbu et al. [3, 18].

SEM analysis of isolated hot spots from reservoir showed that radioactive particles were embedded in residual sediment material. No individual particles containing Pu or U matrix could be extracted.

Based on gamma spectrometry (n=25), ^{137}Cs and ^{241}Am were identified as hot spots. X ray microanalysis spot measurement confirmed the presence of particles containing Sr, as well as Fe, Pb and Ti (Fig. 16). Several heavy metals such as Ce, Mo and Pt were also associated with radioactive particles that also originated from the Mayak plant. In view of the large scale and variety of Mayak operations, there seem to be a variety of different radioactive particles in the reservoir 10 sediments. Sequential extraction experiments have shown that Pu in these sediments is rather inert.

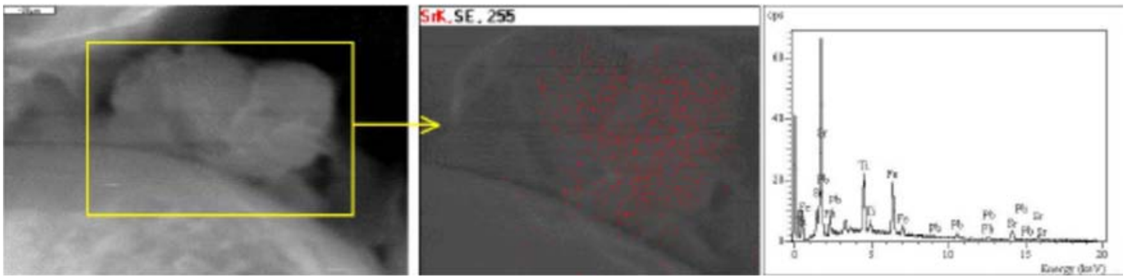

FIG. 16. Scanning electron microscopy of a particle isolated from Mayak reservoir 10 sediments. Secondary electron imaging mode shows the particle embedded in residual sediment material (left, bar 20 µm). X ray mapping reveals that Sr is a major component of the particle matrix (middle) and X ray microanalysis spot measurement confirms the presence of Sr, as well as Fe, Pb and Ti (right) [15].

4.5.2. Sellafield

Among the 3 major European reprocessing plants (Sellafield, Dounreay, La Hague) Sellafield has been the major contributor of actinides to the North European seas. Radioactive particles have been collected and studied by several research groups.

Salbu et al. [181] separated radioactive particles from the Irish Sea sediment at the Ravenglass Estuary, Cumbria. The individual particles were approximately 5−20 µm in size. The matrix of these particles was found to be U, containing about 0.5 Bq ^{241}Am and 0.1 Bq ^{137}Cs (Fig. 17).

Thus, the presence of U fuel particles, presumably originating from Sellafield, has been confirmed. Leaching experiments indicated a high degree of potential mobility and bioavailability.

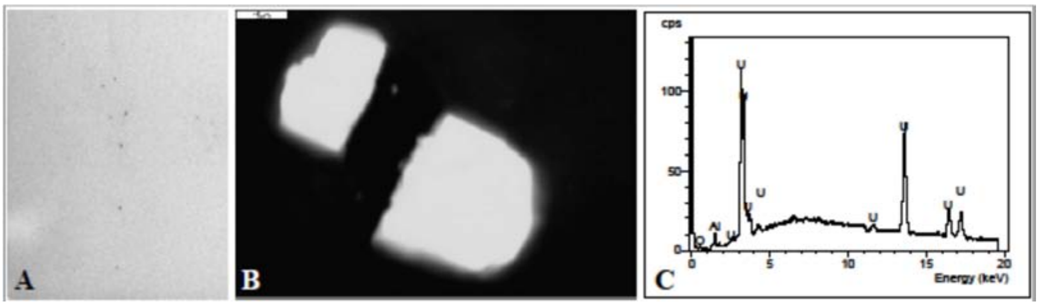

FIG. 17. Ravenglass U fuel particles. (A) Digital autoradiography of Ravenglass surface sediments (0–5 cm). (B) Electron micrograph (BEI mode) of two particles with X ray microanalysis (C) confirming the presence of U. Bar = 5 µm. The appearance of the particles indicates that they were actually one particle which was divided upon manipulation [15].

Radioactive particles with U matrices have also been isolated from Irish Sea sediment cores by Jernström et al. [182]. The origin of these U matrix particles is assumed to be the fuel-rod de-canning process at Sellafield. In one isolated particle only, it was possible to detect traces of Pu by µ-XRF. In two particles, trace amounts of Th were found together with U. According to µ-XANES measurements, U was present in the particles mostly in the less soluble U(IV) form, the ratio of U(VI) to total U content being between 34–40%.

Radioactive particles in the Irish Sea sediment were studied by Hamilton [183] in the 1990s and it was recognized that significant part of the actinide content was attached as coatings to two iron minerals, magnetite and hematite. As a result of the various industrial activities in the Cumbrian coastal region large quantities of hydrated iron oxides and phosphogypsum were discharged into the Irish Sea. Radionuclides associated with colloid and particles were already identified in 1989 in effluent from Sellafield and La Hague by Salbu [20, 37]. The mud patch outside Sellafield is also sufficient enriched with radioactive particles deposited in the sediments. The interaction of the actinides released from Sellafield with the sediment and with deposited industrial wastes resulted in different types of association (with quartz grains, with magnetite and haematite, with barium sulphate). The physico-chemical forms of the actinides, the interaction with organic material as well as the oxidation from PuIII/PuIV to PuV/PuVI will basically determine the present and future remobilization of the actinides.

4.6. RADIOACTIVE PARTICLES FROM DUMPED NUCLEAR WASTES

Radioactive particles were identified in the sediments in Kara Sea and the fjords of Novaya Zemlya during the Russian-Norwegian expeditions in the 1990s [23]. Enhanced levels of fission and activation products (^{137}Cs, ^{60}Co, ^{90}Sr, ^{239,240}Pu) were measured in the sediments in the close vicinity of dumped objects in the fjords of Novaya Zemlya, demonstrating that leakage occurred. Other sources of radioactive contamination in the Kara Sea were identified as global fallout, transport by the Ob and Yenisey rivers, marine transport from Sellafield discharges and fallout from the Chernobyl accident. The general level of contamination in the open Kara Sea was lower than in other adjacent marine systems (e.g. Irish Sea, Baltic Sea).

The radioactive particle collected from the sediments in the Stepovogo Fjord contained ^{60}Co with clay material (Fig. 18). The particle (approx. 10 × 20 µm) contained Fe, Co, Ni, Cr, and Mn together with low atomic number elements. The ^{60}Co bearing particle, being similar to crud particles, may have originated from corrosion of the primary coolant system of a nuclear reactor.

According to the microanalytical studies Cs was attached to large (100 µm) greenish particles that were probably pieces of paint. X ray maps showed the presence of numerous elements, as well as small agglomerated particles (Fig. 19). Ti, a common component of paints, was evenly distributed in the particle. The paint particle might have originated from the storage ships situated at Atomflot.

Three particles were identified on a lichen sample that contained ^{60}Co and Fe, but no U or alpha emitting nuclides were present in the particles. The ^{60}Co-bearing particles were small (1 µm; Fig. 20).

The particles probably originated from the Nerpa Shipyard in the Polarnyy area where the maintenance and repair of nuclear powered ships were performed.

4.7. OTHER TYPES OF RADIOACTIVE PARTICLES

As sophisticated radiochemical and micro-analytical tools became available, more and more particles have been collected and subjected to detailed characterization processes. In particular, radioactive particles associated with various nuclear fuel cycle activities have been investigated.

Indoor nuclear facilities

Radioactive particles are present in nuclear facilities; they are common in nuclear reactors. Two types of radioactive particles have been distinguished in coolant samples of pressurized water reactors by Vajda [185] and Kerkápoly [186]. Particles were collected from the coolant water of NPP Paks, Hungary. Particles containing actinides are typically small (some µm) and a significant part is in the form of colloids.

FIG. 18. SEM image in BEI mode of a particle collected from the sediment in Stepovogo Fjord [23]. X ray measurements revealed the presence of Fe, Ni, Co, Cr, and Mn in addition to ^{60}Co in a 10 × 20 µm particle. Clay particle contained 50 Bq ^{60}Co.

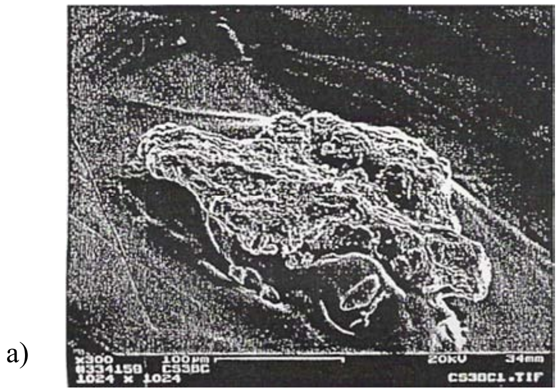

FIG. 19. a) Secondary electron image of a Cs containing particle from the Kola Bay [184]. The particle is attached to adhesive tape.

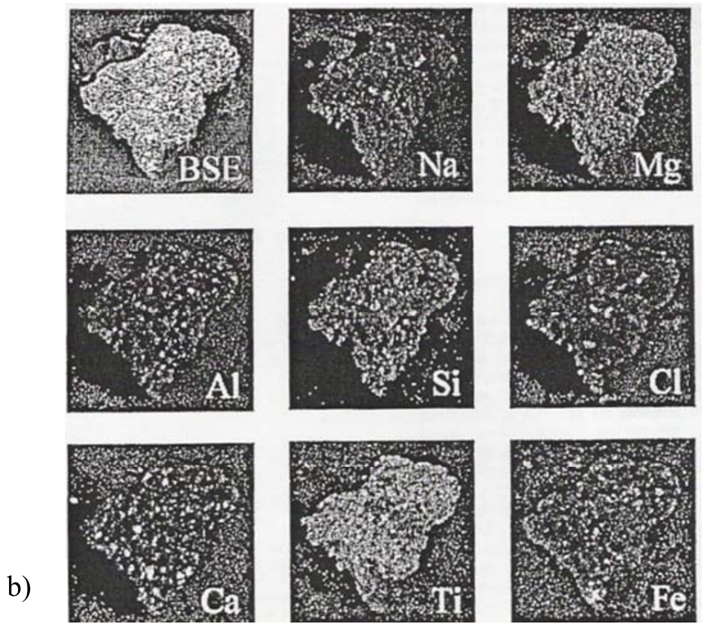

FIG. 19. b) Back scattered electron image and X ray maps of the same particle. Area of the images is 350 × 350 µm^2.

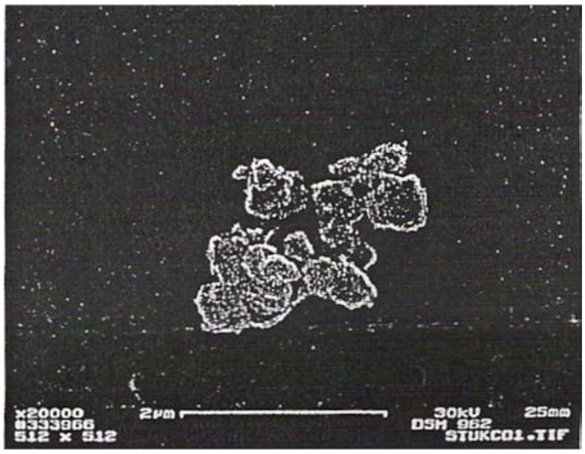

FIG. 20. Secondary electron image of a Co containing particle from the Kola Bay [184]. Scale bar= 2 µm.

Actinides originated either from the surface contamination of the fuel elements or from defected fuels. Analysis of the particles was utilized to identify the source term i.e. the failed fuel element under normal operation conditions. Actinides were identified and analyzed during the reactor incident at NPP Paks in 2003, when several fuel assemblies were destroyed in a loss of coolant accident.

The other type of radioactive particles originating from the coolant consists of activated corrosion products that show a great variety of particle sizes and shapes. Corrosion particles originate from the corrosion processes of the primary circuit materials. The particles are transported by the coolant stream and become activated in the core. Analysis of the corrosion particles contributes to better understanding of corrosion and transport processes in the primary circuit.

NORM/TENORM

Naturally occurring radioactive materials (NORM) or technologically enhanced NORM (TENORM) represent a major source of radioactive particles.

Characteristics of radioactive particles originating from anthropogenic activities can be derived from and traced back to the properties of the natural material. The particle sizes of the natural minerals varied in the range 1–100 μm, where smaller particles (<10 μm) of potential health effect on the respiratory system were more frequent.

Samples of industrially enhanced radioactivity (products, by-products, tailings) as well as natural formations (sediments, rocks, minerals) containing high U and Th concentrations have been studied by Böhnke [68].

Radioactive particles of natural origin have been studied by Selchau-Hansen [187], Böhnke [68] and Alsecz [188]. Radioactive particles of elevated alpha activity were identified in the slag dumps of a former copper production facility (Theisenmud) as well as in the tailings of a former U mine (Dankritz). The presence of airborne radioactive particles in the size range of 1.5 to 2.8 μm was identified in Dankritz samples [188].

Radioactive particles from the tailings of a former U mine and ore processing facility have been collected and analyzed by Alsecz [188]. Oxidation states of individual particles were determined by μ-XANES. Radioactive particles of high U concentration originating from the tailings contained U overwhelmingly (to 50–80%) in the less soluble U(IV) form. Mineralogical composition of the radioactive particles was investigated by μ-diffraction. Similar results have been obtained from U mining sites in Central Asia, where the combination μ-XANES and μ-XRD could reveal the crystalline structure of U within the particles (Salbu, pers. comm.).

A U-containing inclusion in a gem from the collection of the Louvre was also studied using microscopic X ray techniques by Alsecz [188]. The small inclusion in the gem was analyzed at a synchrotron source and the Pb/U ratio was determined. Age calculation helped identify the source of the gem that originates probably from the old mineral India. Based on the measurement of the oxidation state of U it was concluded that 80–85% of U in the bubble of the garnet was in the less mobile U(IV) form.

5. SUMMARY AND CONCLUSIONS

Following serious nuclear events such as nuclear weapon tests or nuclear reactor accidents, refractory radionuclides are mainly released to the environment as radioactive particles, ranging from submicrons to fragments.

The physico-chemical forms of radionuclides associated with particles are different from those present in the form of gases or ionic species of aqueous solutions. The properties of the particle bound radionuclides are governed by the composition and the structure of the matrix, thus mobility, environmental behaviour, bioavailability, ecological and health effects of the radionuclides are basically determined by the properties of the particle [12].

The significance of radioactive particles in environmental contamination and the lack of knowledge about the properties of the particles have been recognized, and the CRP ‘Radiochemical, Chemical and Physical Characterization of Radioactive Particles in the Environment’ was performed during 2001 and 2007 by the IAEA. The present document is an overview with respect to sources that have contributed to radioactive particles in the environment, the analytical techniques available to study radioactive particles, and the properties of individual radioactive particles as they have been determined using the sophisticated techniques. The analytical tools available for research of radioactive particles are given below (Table 9).

The major contributor to radioactive sources in the environment are nuclear explosions, especially atmospheric nuclear weapon tests that had been conducted at several test sites in the 1950s and early 1960s. Accidental as well as authorized releases of radioactive particles from various facilities within the nuclear weapon and fuel cycles have been documented e.g. major reactor accidents and minor reactor incidents, inadvertent destruction of nuclear weapons, releases from reprocessing plants, waste disposal sites, mine and ore processing plants, and dispersal of DU from ammunitions.

Radioactive particles in the environment have been detected since the early times of their releases. Radioactive particles originating from atmospheric tests were studied intensively during the 1950s and 1960s. Particle sizes, distributions, radioactivity of the particles were determined and the basics of fractionation phenomena were evaluated. In the 1970s and 1980s, comprehensive environmental survey programs of the former weapons test sites were initiated all around the world, where the special role of radioactive particles in environmental contamination was mostly ignored. In 1986, a significant amount of radioactive material was dispersed in Europe due to the Chernobyl accident contaminating densely populated areas, and the particle issue became essential. In parallel with the development of radio- and microanalytical techniques, comprehensive investigations of individual radioactive particles originating from various sources have been performed. The present document was intended to give an overview about the recent achievements of the studies.

Individual radioactive particles originating from the former weapons test sites (Marshall Islands, Mururoa, Semipalatinsk, Novaya Zemlya), from the Chernobyl accident (exclusion zone and various locations in Europe), from the inadvertent destruction of nuclear bombs (Palomares and Thule), from DU ammunition (Kosovo, Kuwait), from the environment of reprocessing plants (Mayak, Sellafield), and from a dumping site of radioactive waste (Kara Sea) have been characterized in detail. General conclusions were drawn about the different types of sources, and individual signatures of the particles were determined. A data bank of radioactive particles originating from the Chernobyl accident has been established.

Based on a series of investigations, the composition of particles seems to reflect the emitting source, while particle characteristics such as size, crystalline structure and oxidation state depend on the release scenario [12, 15, 189]. Such characteristics affect particle weathering rates and remobilisation of particle associated radionuclides, and thereby ecosystem transfer, biological uptake and effect. The CRP participants concluded that a follow-up CRP should focus on addressing the knowledge gaps associated with ecosystem transfer as well as potential biological effects caused by the presence of radioactive particles.

TABLE 9. ANALYTICAL TOOLS USED TO STUDY RADIOACTIVE PARTICLES

Method	Information obtained
Particle identification	
Size fractionation in soil and sediments by sieving followed by radioanalytical techniques	Size distribution
Size fractionation in water by in situ filtration and ultrafiltration followed by radioanalytical techniques	Size distribution
Cascade impactor with aerosol filters followed by radioanalytical techniques	Size distribution (AMAD)
Repeated sample splitting combined with radioanalytical techniques	Identification of the presence of RPs
Repeated sample mixing combined with radioanalytical techniques	Identification of the presence of RPs (skewed frequency distribution)
Portable monitors in the field	Identification of hot spots
Autoradiography	Distribution of radioactive material
Solid state nuclear track detection	Distribution of radioactive material
Real time imaging techniques	Distribution of radioactive material

TABLE 9. ANALYTICAL TOOLS USED TO STUDY RADIOACTIVE PARTICLES (Cont.)

Method	Information obtained
SEM-EDX, SEM-WDX, EPMA	Elemental distribution
μ-XRF mapping	Elemental distribution
Particle isolation	
Micromanipulation under light microscope	
Micromanipulation under SEM	
Micromanipulation using atomization techniques	
Micro-surgery of particles	
Particle characterisation	
γ spectrometry, X ray spectrometry	Radionuclide activity concentrations
β spectrometry (LSC)	Radionuclide activity concentrations
α spectrometry	Radionuclide activity concentrations
SEM-EDX, SEM-WDX, EPMA	Size distribution, surface morphology, elemental composition, distribution
TEM, STEM-EDX	Size distribution, surface morphology, elemental composition, distribution
EELS	Elemental composition (low atomic number), chemical bonding
μ-PIXE	Elemental distribution
μ-XRF , μ-SRXRF	Elemental distribution (2D)
Confocal μ-XRF	Elemental distribution (3D)
μ-XRD	Morphology, crystallographic structures
EXAFS	Structure of non crystalline materials
μ-XANES	Oxidation state (distribution)
μ-tomography	Spatial distribution of density, elements
Mass spectrometry (SIMS, ICP-MS, AMS, RIMS)	Elemental and isotope composition
LA-ICP-MS, LAMMA	Elemental and isotope composition
Activation analysis	Trace element composition
IR and Raman spectrometry	Chemical bonding

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ABBREVIATIONS

μ-XRD	X ray microdiffraction
AMAD	activity median aerodynamic diameter
AMS	accelerator mass spectrometry
BSE	back-scattered electrons
CMT	computed microtomography
CRP	Coordinated research project
DU	Depleted uranium
EDX	energy-dispersive X ray analyser
EELS	electron energy loss spectroscopy
EPMA	electron probe microanalysis
ERD	elastic recoil detection technique
ESCA	electron spectroscopy for chemical analysis
EXAFS	extended X ray absorption fine structure analysis
FAST	forward angle scattering technique
FIB	focused ion beam
FT IR	Fourier transformation infrared
FT LAMMA	Fourier Transform laser microprobe mass spectrometry
FT LMMS	Fourier Transform laser microprobe mass spectrometry
FTA	fission track analysis
HP	hot particles
ICP-MS	inductively coupled plasma mass spectrometry
ICP-SF-MS	inductively coupled sector field plasma mass spectrometry
IDE	integrated detector & electronics (bioscope)
IR	infrared spectroscopy
LASER	light amplification by stimulated emission of radiation
LAMMA	laser microprobe mass analysis
MS	mass spectrometry
NAA	neutron activation analysis
NORM	naturally occurring radioactive material
NTD	nuclear track detection
OES	emission spectroscopy
PIXE	particle induced X ray emissions
POI	particle of interest
RIMS	resonance ionization mass spectrometry
RP	radioactive particles

RTDI	real-time digital imaging systems
SAED	sample area electron diffraction
SAM	scanning auger microscopy
SE	secondary electrons
SEM	scanning electron microscopy
SEM-EDX	scanning electron microscopy based on energy-dispersive detection of emitted characteristic X rays
SEM-WDX	scanning electron microscopy based on wavelength detection of emitted characteristic X rays
SIMS	secondary ionization mass spectrometry
SSNTD	solid state nuclear track detection
SRXRF	Synchrotron radiation X ray fluorescence
STEM	scanning transmission electron microscopy
STIM	scanning transmission ion microscopy
TEM	transmission electron microscopy
TENORM	technologically enhanced naturally occurring radioactive material
TLD	Thermoluminescent dosimetry
TMI	Three Mile Island
TOF	time of flight
TQSA	total quantitative scanning analysis
XAFS	X ray absorption fine structure analysis
XANES	X ray absorption near-edge structure
XRD	X ray diffraction
XRF	X ray fluorescence

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