



IAEA

International Atomic Energy Agency

IAEA TECDOC SERIES

No. 2061

A Practical Guide to Advanced Radio-Krypton Groundwater Dating

Technical Synthesis of a Coordinated Research Project

A PRACTICAL GUIDE
TO ADVANCED RADIO-KRYPTON
GROUNDWATER DATING

The following States are Members of the International Atomic Energy Agency:

| | | |
|-------------------------------------|-------------------------------------|--|
| AFGHANISTAN | GERMANY | PALAU |
| ALBANIA | GHANA | PANAMA |
| ALGERIA | GREECE | PAPUA NEW GUINEA |
| ANGOLA | GRENADA | PARAGUAY |
| ANTIGUA AND BARBUDA | GUATEMALA | PERU |
| ARGENTINA | GUINEA | PHILIPPINES |
| ARMENIA | GUYANA | POLAND |
| AUSTRALIA | HAITI | PORTUGAL |
| AUSTRIA | HOLY SEE | QATAR |
| AZERBAIJAN | HONDURAS | REPUBLIC OF MOLDOVA |
| BAHAMAS | HUNGARY | ROMANIA |
| BAHRAIN | ICELAND | RUSSIAN FEDERATION |
| BANGLADESH | INDIA | RWANDA |
| BARBADOS | INDONESIA | SAINT KITTS AND NEVIS |
| BELARUS | IRAN, ISLAMIC REPUBLIC OF | SAINT LUCIA |
| BELGIUM | IRAQ | SAINT VINCENT AND THE GRENADINES |
| BELIZE | IRELAND | SAMOA |
| BENIN | ISRAEL | SAN MARINO |
| BOLIVIA, PLURINATIONAL STATE OF | ITALY | SAUDI ARABIA |
| BOSNIA AND HERZEGOVINA | JAMAICA | SENEGAL |
| BOTSWANA | JAPAN | SERBIA |
| BRAZIL | JORDAN | SEYCHELLES |
| BRUNEI DARUSSALAM | KAZAKHSTAN | SIERRA LEONE |
| BULGARIA | KENYA | SINGAPORE |
| BURKINA FASO | KOREA, REPUBLIC OF | SLOVAKIA |
| BURUNDI | KUWAIT | SLOVENIA |
| CABO VERDE | KYRGYZSTAN | SOUTH AFRICA |
| CAMBODIA | LAO PEOPLE'S DEMOCRATIC REPUBLIC | SPAIN |
| CAMEROON | LATVIA | SRI LANKA |
| CANADA | LEBANON | SUDAN |
| CENTRAL AFRICAN REPUBLIC | LESOTHO | SWEDEN |
| CHAD | LIBERIA | SWITZERLAND |
| CHILE | LIBYA | SYRIAN ARAB REPUBLIC |
| CHINA | LIECHTENSTEIN | TAJIKISTAN |
| COLOMBIA | LITHUANIA | THAILAND |
| COMOROS | LUXEMBOURG | TOGO |
| CONGO | MADAGASCAR | TONGA |
| COSTA RICA | MALAWI | TRINIDAD AND TOBAGO |
| CÔTE D'IVOIRE | MALAYSIA | TUNISIA |
| CROATIA | MALI | TÜRKİYE |
| CUBA | MALTA | TURKMENISTAN |
| CYPRUS | MARSHALL ISLANDS | UGANDA |
| CZECH REPUBLIC | MAURITANIA | UKRAINE |
| DEMOCRATIC REPUBLIC OF THE CONGO | MAURITIUS | UNITED ARAB EMIRATES |
| DENMARK | MEXICO | UNITED KINGDOM OF GREAT BRITAIN AND NORTHERN IRELAND |
| DJIBOUTI | MONACO | UNITED REPUBLIC OF TANZANIA |
| DOMINICA | MONGOLIA | UNITED STATES OF AMERICA |
| DOMINICAN REPUBLIC | MONTENEGRO | URUGUAY |
| ECUADOR | MOROCCO | UZBEKISTAN |
| EGYPT | MOZAMBIQUE | VANUATU |
| EL SALVADOR | MYANMAR | VENEZUELA, BOLIVARIAN REPUBLIC OF |
| ERITREA | NAMIBIA | VIET NAM |
| ESTONIA | NEPAL | YEMEN |
| ESWATINI | NETHERLANDS, KINGDOM OF THE | ZAMBIA |
| ETHIOPIA | NEW ZEALAND | ZIMBABWE |
| FIJI | NICARAGUA | |
| FINLAND | NIGER | |
| FRANCE | NIGERIA | |
| GABON | NORTH MACEDONIA | |
| GAMBIA | NORWAY | |
| GEORGIA | OMAN | |
| | PAKISTAN | |

The Agency's Statute was approved on 23 October 1956 by the Conference on the Statute of the IAEA held at United Nations Headquarters, New York; it entered into force on 29 July 1957. The Headquarters of the Agency are situated in Vienna. Its principal objective is "to accelerate and enlarge the contribution of atomic energy to peace, health and prosperity throughout the world".

IAEA-TECDOC-2061

A PRACTICAL GUIDE
TO ADVANCED RADIO-KRYPTON
GROUNDWATER DATING

TECHNICAL SYNTHESIS
OF A COORDINATED RESEARCH PROJECT

INTERNATIONAL ATOMIC ENERGY AGENCY
VIENNA, 2024

COPYRIGHT NOTICE

All IAEA scientific and technical publications are protected by the terms of the Universal Copyright Convention as adopted in 1952 (Berne) and as revised in 1972 (Paris). The copyright has since been extended by the World Intellectual Property Organization (Geneva) to include electronic and virtual intellectual property. Permission to use whole or parts of texts contained in IAEA publications in printed or electronic form must be obtained and is usually subject to royalty agreements. Proposals for non-commercial reproductions and translations are welcomed and considered on a case-by-case basis. Enquiries should be addressed to the IAEA Publishing Section at:

Marketing and Sales Unit, Publishing Section
International Atomic Energy Agency
Vienna International Centre
PO Box 100
1400 Vienna, Austria
fax: +43 1 26007 22529
tel.: +43 1 2600 22417
email: sales.publications@iaea.org
www.iaea.org/publications

For further information on this publication, please contact:

Isotope Hydrology Section
International Atomic Energy Agency
Vienna International Centre
PO Box 100
1400 Vienna, Austria
Email: Official.Mail@iaea.org

© IAEA, 2024
Printed by the IAEA in Austria
July 2024

IAEA Library Cataloguing in Publication Data

Names: International Atomic Energy Agency.
Title: A practical guide to advanced radio-krypton groundwater dating : technical synthesis of a coordinated research project / International Atomic Energy Agency.
Description: Vienna : International Atomic Energy Agency, 2024. | Series: IAEA TECDOC series, ISSN 1011-4289 ; no. 2061 | Includes bibliographical references.
Identifiers: IAEAL 24-01694 | ISBN 978-92-0-122924-3 (paperback : alk. paper) | ISBN 978-92-0-122824-6 (pdf)
Subjects: LCSH: Groundwater — Technological innovations. | Groundwater — Testing. | Hydrogeology. | Fossils.

FOREWORD

The increasing global demand for water and the impacts of pollution and climate change on surface waters have driven the growing reliance on groundwater for agriculture, domestic and industrial uses. Shallow aquifers are initially tapped in conjunction with other water sources, but their intense exploitation often leads to negative consequences, such as declining water tables, degraded water quality and environmental impacts. As a result, deeper aquifers containing older groundwater are increasingly being explored as a viable alternative. Understanding the origin, history and dynamics of these deep groundwater resources is crucial for assessing their reliability and potential as long term water supplies.

To determine the age of groundwater extracted from deep aquifers, isotope methods and groundwater flow modelling are commonly used. Traditionally, radiocarbon and tritium have been used to estimate groundwater age, but their limitations restrict accurate dating beyond approximately 40 000 years. Recent advancements have introduced alternative isotopes, such as chlorine-36 and uranium isotopes, as more reliable age indicators, although their widespread use remains limited. The accumulation of helium-4 in deep groundwater has also been proposed as a dating method, but its calibration requires the use of other radionuclides or age indicators.

In this context, significant progress has been made in analytical methods for determining dissolved noble gases and trace-level noble gas radionuclides in groundwater. Atom trap trace analysis has revolutionized the measurement of extremely low concentrations of exotic radionuclides, including krypton-81, offering a valuable tool for estimating groundwater ages in deep aquifers. Krypton-81 is an ideal tracer because of its long half-life and minimal geochemical interactions in the aquifer. Moreover, krypton-81 results enable the calibration of groundwater ages derived from helium-4 accumulation, overcoming previous inaccuracies associated with carbon-14's shorter half-life.

This publication provides detailed information on recent technical advancements and operational procedures achieved through the coordinated research project entitled Use of Long-lived Radionuclides for Dating Very Old Groundwaters. It covers field portable membrane gas extraction devices for sampling dissolved gases from groundwater aquifers, as well as a custom built krypton purification system for purifying krypton from field collected bulk gas samples. Additionally, the publication offers information on selecting appropriate groundwater wells and sampling tools, as well as information for proper sample handling and transportation. This information is essential to ensure smooth field sampling, which is vital for accurate isotope analysis and data interpretation.

The IAEA wishes to thank all the contributors involved in the preparation of this publication. The IAEA officer responsible for this publication was T. Matsumoto of the Division of Physical and Chemical Sciences.

EDITORIAL NOTE

This publication has been prepared from the original material as submitted by the contributors and has not been edited by the editorial staff of the IAEA. The views expressed remain the responsibility of the contributors and do not necessarily represent the views of the IAEA or its Member States.

Guidance and recommendations provided here in relation to identified good practices represent expert opinion but are not made on the basis of a consensus of all Member States.

Neither the IAEA nor its Member States assume any responsibility for consequences which may arise from the use of this publication. This publication does not address questions of responsibility, legal or otherwise, for acts or omissions on the part of any person.

The use of particular designations of countries or territories does not imply any judgement by the publisher, the IAEA, as to the legal status of such countries or territories, of their authorities and institutions or of the delimitation of their boundaries.

The mention of names of specific companies or products (whether or not indicated as registered) does not imply any intention to infringe proprietary rights, nor should it be construed as an endorsement or recommendation on the part of the IAEA.

The authors are responsible for having obtained the necessary permission for the IAEA to reproduce, translate or use material from sources already protected by copyrights.

The IAEA has no responsibility for the persistence or accuracy of URLs for external or third party Internet web sites referred to in this publication and does not guarantee that any content on such web sites is, or will remain, accurate or appropriate.

CONTENTS

| | | |
|--------|---|----|
| 1. | INTRODUCTION..... | 1 |
| 1.1. | BACKGROUND | 1 |
| 1.2. | OBJECTIVE | 2 |
| 1.3. | SCOPE..... | 3 |
| 1.4. | STRUCTURE..... | 3 |
| 2. | RECENT DEVELOPMENT OF ATTA AND RECOMMENDATION FOR FIELD SAMPLING METHODOLOGY | 5 |
| 2.1. | GAS SAMPLING AND SHIPMENT | 5 |
| 2.2. | INSTRUCTIONS FOR SAMPLING BACK UTILIZATION..... | 6 |
| 2.3. | ADDITIONAL NOTES | 7 |
| 3. | SELECTION OF SAMPLING SITE FOR ^{81}KR AGE DATING BASED ON ^4HE CONCENTRATION | 9 |
| 3.1. | ^4HE AS A GROUNDWATER AGE PROXY | 9 |
| 3.2. | SOURCE OF THE TERRIGENIC HELIUM COMPONENT | 10 |
| 3.3. | EXPLORING THE POTENTIAL AGE RANGE INFERRED FROM ^4HE | 11 |
| 4. | SAMPLING METHODOLOGY FOR GROUNDWATER AGE DATING WITH ^{81}KR | 15 |
| 4.1. | FIELD DEGASSING DEVICE..... | 15 |
| 4.2. | STANDARD OPERATING PROCEDURE OF IAEA-EDGAR-MK I..... | 17 |
| 4.2.1. | Water Flow Connection | 18 |
| 4.2.2. | Gas Flow Connection..... | 21 |
| 4.2.3. | Gas Sampling Procedure..... | 26 |
| 4.3. | STANDARD OPERATING PROCEDURE OF IAEA-EDGAR-MK II..... | 30 |
| 4.3.1. | Preparation of the device | 31 |
| 4.3.2. | Gas Flow Connection..... | 34 |
| 4.3.3. | Flushing | 36 |
| 4.3.4. | Purging..... | 37 |
| 4.3.5. | Sample Gas Collection..... | 38 |
| 5. | KRYPTON PURIFICATION FOR ATTA..... | 41 |
| 5.1. | SYSTEM CONFIGURATION..... | 41 |
| 5.2. | CRYOGENIC DISTILLATION | 42 |
| 5.3. | GAS CHROMATOGRAPHY | 43 |
| 5.4. | METHANE REMOVAL METHOD..... | 45 |
| 6. | DATA REDUCTION IN ^{81}KR ANALYSIS OF GROUNDWATER SAMPLES.. | 47 |

| | | |
|------|---|----|
| 6.1. | AGE CALCULATION..... | 47 |
| 6.2. | AGE CORRECTION | 47 |
| 6.3. | ATMOSPHERIC HISTORY OF ⁸¹ KR | 48 |
| 6.4. | ERROR ESTIMATION | 48 |
| 6.5. | SUMMARY..... | 49 |
| | REFERENCES..... | 51 |
| | LIST OF ABBREVIATIONS | 57 |
| | CONTRIBUTORS TO DRAFTING AND REVIEW | 59 |

1. INTRODUCTION

1.1. BACKGROUND

Globally, freshwater is increasingly used for agriculture, industry, and other domestic purposes. Demand is further exacerbated by impacts of pollution and climate change on rivers, lakes, and other water sources [1, 2]. Increase of demand and subsequent stress on freshwater availability is pushing authorities to rely on alternative groundwater sources such as shallow groundwater aquifers which are more recently recharged. This phenomenon takes place alongside the exploitation of surface water sources like rivers and lakes, which are typically the initial targets of utilization [3-5]. Such swift and extensive reliance on shallow groundwater aquifers frequently results in a decline in groundwater levels, degradation of water quality, and soil subsidence, among various other adverse environmental effects [6-9]. Thus, the subsequent exploration and exploitation of deeper and older groundwater aquifers, recharged over thousands of years and from large catchment areas, is expected. A proper understanding of origin, history, and hydrodynamics are essential for the assessment and reliability for old, or ‘paleo’ ground waters as resources for the future supply of water.

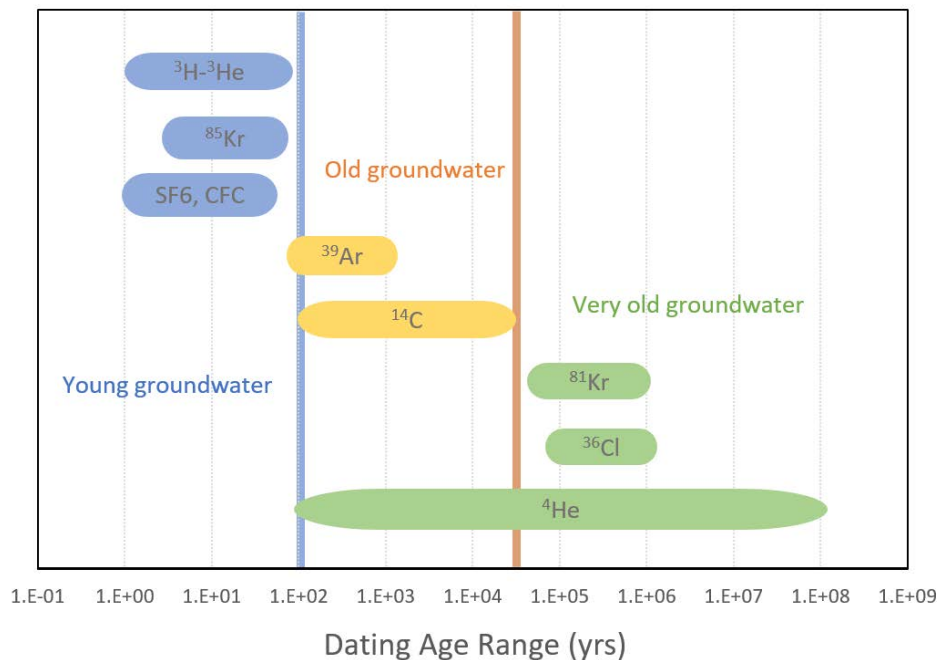


FIG. 1. Dating time ranges for isotopic age tracers. ^4He is potentially capable to cover most of expected groundwater ages in the domain of “(very) old” groundwater in deep aquifer systems.

The common method for determining sustainable groundwater yield in deep aquifers involves estimating groundwater age by combining isotope techniques with groundwater flow modeling [10, 11]. The age of groundwater is thus an essential parameter to be quantified and becomes especially important in arid zone aquifers. Demand on water resources is high in these environments, while low ground water recharge dramatically decreases availability of renewable reserves [12, 13]. For over half a century, isotope hydrology studies have commonly utilized radiocarbon (^{14}C) and tritium (^3H) to provide preliminary groundwater age estimates

(Fig. 1). Given the half-life of ^{14}C at 5,730 years and the intricate geochemistry of carbon forms in various settings, this tracer's use has been restricted to waters relatively young, up to 40,000 years old. In recent times, several other isotopes and long-lived radionuclides have been experimented with to broaden the dating spectrum for groundwater. Of these, chlorine-36 (^{36}Cl), with a half-life of 300,000 years, has been applied with varied outcomes, largely due to challenges associated with in-situ production. Uranium isotopes ($^{234}\text{U}/^{238}\text{U}$) have also been tested, but it is rarely the case that these give meaningful age estimates as their activity ratios are often disturbed by water-rock interactions [14, 15]. Transportation and accumulation of radiogenic helium (^4He) produced by the decay of uranium ($^{235}, ^{238}\text{U}$) and thorium (^{232}Th) in continental basement rock has also been used. ^4He has the potential to date groundwater with a range of residence time from centuries to potentially millions of years, yet the occurrence of sources external to aquifers (basal fluxes entering the bottom of aquifers) or misunderstanding of release rates from rock to water have often hampered its use. Generally, the (U-Th)/ ^4He method requires calibration of the transfer rates by other radionuclides or age indicators (e.g., [16]).

1.2. OBJECTIVE

Recent advancements in analytical techniques have enabled the accurate measurement of dissolved noble gases and trace amounts of noble gas radionuclides in groundwater [17-19]. The Atom Trap Trace Analysis (ATTA) method has seen significant enhancements recently. It can now handle minimal amounts of noble gases, offering the potential for routine measurements of very low radionuclide concentrations in groundwater, like ^{81}Kr (^{81}Kr ; half-life 229,000 years). ATTA involves the selective capture of individual atoms of a given isotope using six laser beams.

After a bulk groundwater, seawater, or ice sampling and subsequent purification (degassing and proper transport), the ATTA method works as follows: A magneto-optical trap captures a neutral atom of a specific isotope, and its presence is detected by observing its fluorescence. By tuning the laser frequency to the resonance of the targeted species, such as ^{81}Kr , it is possible for a specific isotope to be captured by the magneto-optical trap. In this way, the method is unique among all trace analysis methods as its detection does not allow for interference from other elements present (University of Science & Technology of China). Until recently, ^4He ages were calibrated using ^{14}C ages to account for the basal helium flux. However, due to the relatively short half-life of ^{14}C , this method often yielded inaccurate age estimates for groundwater older than 40,000 years. The ^{81}Kr results offer the possibility of calibrating groundwater ages in the range of 45,000-1,200,000 years derived from the ^4He accumulation method.

The Isotope Hydrology Laboratory (IHL) of the International Atomic Energy Agency (IAEA) assists member states in managing water resources by offering groundwater age dating expertise. This is achieved through the Tritium-Helium-3 method (see references (e.g., [20-25]) and the ^4He method (e.g., [16, 26, 27]). IHL is making significant progress in sample collection and purification, enhancing the application of radio-Krypton dating. These initiatives are designed to enhance the management of groundwater resources within the member states of the IAEA. This endeavour is a collaborative effort, involving scientists from Member States through the agency's Coordinated Research Project (CRP) titled "Use of Long-Lived Radionuclides for Dating Very Old Groundwater" which spanned from 2016 to 2022. The primary aim of this CRP had been to explore the application of long-lived radionuclides,

especially ^4He and ^{81}Kr , to evaluate their effectiveness as age tracers for 'old' groundwaters. The groundwater ages determined using these long-lived radionuclide tracers had been contrasted with ages derived from conventional isotopic and hydrochemical tracers across diverse hydrogeological and climatic settings.

During the CRP, 14 Member States were actively involved, conducting thorough groundwater sampling and isotope analysis in specific aquifer systems. Over the project's five-year duration, the CRP amassed over 600 stable noble gas data points and 90 ATTA ^{81}Kr data sets. These data served four main objectives:

- Assessing the effectiveness of long-lived radionuclides in deep groundwater systems for determining groundwater ages.
- Evaluating the efficiency of various sampling techniques and analytical methods for long-lived radionuclides.
- Using the data to compare ^4He results with other age indicators, to decipher the factors influencing ^4He accumulation rates in aquifers from diverse hydrogeological contexts (such as comparing ^4He with ^{81}Kr).
- Utilizing the data to investigate the relationship between long-lived radionuclides and standard hydrochemical tracers, to better understand their physical and chemical interactions in different hydrogeological settings.

1.3. SCOPE

This publication's goal is to deliver comprehensive details about the technical advancements made through the CRP. It particularly focuses on the latest technical progress and operational procedures related to field-portable membrane gas extraction devices, which are used to sample dissolved gases from groundwater aquifers. Additionally, it covers a krypton purification system designed for refining krypton from bulk gas samples collected in the field. It's important to note that these devices are custom-made in laboratories and are not available on the commercial market.

Furthermore, this publication provides general guidelines for selecting appropriate groundwater wells and sampling tools and expectations for proper sample handling and transportation to ensure flawless field sampling, which is a prerequisite for successful isotope analysis and subsequent data interpretation. Overall, this information is intended to facilitate the field sampling process and ensure the accurate interpretation of the data obtained.

1.4. STRUCTURE

This publication is organized in six sections.

Section 1 presents the background, purpose and intended use, as well as the scope and structure of this publication.

Chapter 2 provides an overview of the recent advancements in the field ATTA for the analysis of ^{81}Kr and ^{85}Kr isotopes. It discusses the establishment of ATTA systems for routine analysis at different institutions and the progress made in reducing sample sizes for ^{81}Kr analysis. The section also covers important aspects of field sampling methodology, including well inspection, gas sampling, and shipment procedures. It emphasizes the need for proper sample handling, recommended sampling containers, gas extraction systems, and considerations for sample shipment. Additionally, it provides guidelines for using gas sampling bags and highlights the importance of sample information documentation for accurate processing and analysis.

Section 3 focuses on the use of ^4He as a tracer for estimating groundwater age and screening potential sampling sites for ^{81}Kr age dating. It begins by emphasizing the challenges and specialized equipment required for ATTA analysis and the preparation of gas samples. The section then explains how the concentration of ^4He in groundwater can serve as an age proxy and discusses its relationship with groundwater residence time. A wide range of ^4He concentrations observed in groundwater samples from different aquifers is presented, with examples of recent recharge and the accumulation of terrigenous ^4He over extended periods. The source of terrigenous helium and its identification using a three-isotope diagram are discussed, along with the presence of mantle-helium and its influence on the ^3He budget. The section also explores the correlation between ^4He concentrations and radiocarbon ages, highlighting the limitations of radiocarbon dating beyond a certain range. Additionally, the section mentions the use of a portable mass spectrometer system for field determination of helium concentrations to assess the suitability of potential sites for ^{81}Kr dating.

Section 4 provides a detailed guide to the sampling methodology for groundwater age dating using ^{81}Kr . It explains the principles and configuration of the field degassing device that performs Extraction of Dissolved Gases for Analysis of Radiokrypton (EDGAR) and presents the standard operating procedure for the IAEA-EDGAR-Mk I sampler. The section also highlights the advancements in sampling techniques and the development of the second-generation IAEA-EDGAR-Mk II sampler with its comprehensive standard operating procedure.

Section 5 explores the purification of krypton for ATTA. It presents an overview of the krypton purification system developed at the IHL, highlighting the cryogenic distillation, gas chromatography (GC), and final purification stages. The section also discusses the methane removal method used to eliminate methane from the gas sample. Overall, it provides insights into the process of obtaining a pure krypton sample for analysis.

Section 6 focuses on the data reduction process for ^{81}Kr analysis of groundwater samples using ATTA. It outlines the protocol for age calculation based on the measured ^{81}Kr abundance and the half-life of ^{81}Kr . The section also discusses the correction for atmospheric contamination and the estimation of errors. Furthermore, it explores the atmospheric history of ^{81}Kr and its impact on age calculations. The sources of uncertainty are identified, including statistical errors, systematic error, and additional uncertainties from the correction procedure.

2. RECENT DEVELOPMENT OF ATTA AND RECOMMENDATION FOR FIELD SAMPLING METHODOLOGY

Two ATTA instruments are currently operating for routine analysis of ^{81}Kr and ^{85}Kr , one at the University of Science and Technology of China (USTC) and one at the Argonne National Laboratory (ANL). Moreover, an ATTA system for routine analysis of ^{81}Kr and ^{85}Kr has been set up at the Australian Facility for Noble-Gas Radio Isotope Measurements at the University of Adelaide. First $^{81}\text{Kr}/^{85}\text{Kr}$ results for groundwater samples have been obtained from this ATTA system and the commissioning for routine operation is expected for early 2023.

Besides the ATTA systems for routine operation, there are three ATTA systems (2 at USTC, 1 at ANL) for research and development with the goal to reduce the uncertainty and required sample size for ^{81}Kr analysis. In 2019 a Kr81- and an Ar39-ATTA instrument have been commissioned at USTC. An Ar39-ATTA instrument is also planned at the University of Adelaide.

Sample size requirements for the current, third generation ATTA instruments used at both analysis laboratories range from 2 to 5 μL (Standard Temperature and Pressure (STP)) of krypton gas for a single measurement. Smaller sample sizes of 0.5 to 2 μL are acceptable but will lead to increased statistical and systematic uncertainties in extracted ^{81}Kr concentrations. Ideally, sample sizes should allow duplicate measurements in support of quality control and should be between 5 to 10 μL total. Using the R&D ATTA systems, substantial progress has been made on reducing the sample size for ^{81}Kr analysis from 20 kg of water to ~ 5 kg of water. The analysis of ^{81}Kr in 100 nL of krypton (corresponding to ~ 2 kg of water) could be demonstrated.

Krypton purification systems are operating at USTC (China), IHL (IAEA), CSIRO (Australia), Argonne (USA) and University of Chicago (USA). USTC has a fully automated system operational capable of handling up to 5 samples per day. A second system has been completed at USTC in 2021 to meet the increasing demand. The krypton purification system at IHL has been rebuilt in 2021 and tested using $^{81}\text{Kr}/^{85}\text{Kr}$ analysis in laboratory air and groundwater samples [28]. Sample processing should be coordinated geographically to distribute the workload and simplify logistics.

Compressed gas samples containing large amounts of gases other than N_2 , e.g., methane or CO_2 , need special treatment. The field teams should notify the separation labs early if those conditions are present. The separation labs are prepared to handle those samples, but additional purification procedures are needed for processing. Methane-rich gas samples are particularly difficult to ship due to the combustion hazard. At CRIEPI (Japan) a system for methane removal has been developed to pre-process methane-rich gas-samples extracted from groundwater (Section 5), facilitating shipping to USTC for ^{81}Kr analysis.

2.1. GAS SAMPLING AND SHIPMENT

Accessibility and well conditions need to be carefully considered for suitability of ^{81}Kr sampling. Initially, the well headwork should be inspected for air tightness, then flushed (> 3 times the well volume) before sampling to avoid air contamination. Flow rate and temperature should be checked thoroughly before sampling. Ideally the flow rate should be > 3 L/min, and

if temperatures reach $> 50\text{ }^{\circ}\text{C}$, additional cooling units for water are required to ensure normal operations of the gas extraction system. Furthermore, the composition of dissolved gases should be checked before sampling operations. High concentration gases other than N_2 (e.g., CH_4 , CO_2 , and H_2S) need special procedures. Thus, as a minimum the sample volume needs to be raised accordingly.

Gas extraction systems will be provided to the field-teams by the regional gas processing labs, and Field teams need to be trained on the specific units before sampling operation. Further, field team operators should acquire appropriate sample container(s), such as ‘Multi-Layer Foil’ gas sampling bags with screw cap valve (Supel Inert Multi-Layer Foil gas sampling bags from Sigma-Aldrich or bags with similar construction). These are now recommended as the preferred method for samples that don’t contain a lot of methane, due to easy handling and shipping. As for methane-rich samples, it is recommended to use aluminum gas cylinders with standardized connectors from recommended, specified vendors that meet respective standards (DOT, EU, or equivalent).

- Before each sample extraction, check the leak rate with an empty cylinder (This step is not necessary for gas bags since they come deflated). Then, flush gas extraction unit with dissolved gases. Extract required gas volume not exceeding flow rate specified for sampling unit (For gas bags fill it to 50%-60% of its maximum volume).
- DO NOT fill bag to its maximum volume, this is because extra room is needed for the gas to expand when the sample is shipped by airplane (see details about how to use sampling bags in the last section of 2.3.1). Teams should also perform maintenance procedures of gas extraction unit after sampling.
- Note that if salinity of the well water is high, the extraction unit needs to be flushed with fresh water right after sampling.
- Extraction of an air sample will be representative of the regional ^{85}Kr concentration. This can help in correction of potential air contamination during sampling. It is recommended to take one such sample during each sampling operation. This sample can be taken by exposing a pre-evacuated gas cylinder to the air or by filling a gas sampling bag with air. Respective sample size of 4 L air (STP) is sufficient.

Gas extraction systems have been developed at various laboratories and tend toward more compact and easier to use units. As of now, typical compact units can tolerate flow rates of between 5 to 20 L/min. The extracted gases (5 – 6 L STP) are typically collected in a 10 L gas bag or compressed into aluminum gas cylinders of approximately 4 L volume and pressures up to 1.5 bar. These sample requirements are with respect to N_2 equivalent. If the extracted gas contains large concentration of CO_2 or methane, sample sizes need to be respectively larger, requiring more than one cylinder. This is to ensure enough krypton is present. We therefore recommend early analysis of gas composition. Gas purification procedures will also depend on this gas composition. In special cases, on-site removal of contaminant gases (e.g., CO_2) can be a preferable option. Finally, to ensure consistent and reliable data, it is recommended to use a database accessible to the program participants.

2.2. INSTRUCTIONS FOR SAMPLING BACK UTILIZATION

This instruction guide utilizes the ‘Supel™ Inert Multi-Layer Foil’ gas sampling bags from Sigma-Aldrich as an example (Fig. 2), however, sampling bags with similar construction from other companies should work equally well.

- First, connect the inlet of the gas bag and the outlet of the gas extraction device with a transparent flexible plastic tube. To get good seal, the inner diameter of the tube should be slightly smaller than the outer diameter of the gas inlet of the gas bag. Soft transparent plastic tubing (For example PVC tubing) is recommended. Use tube clamps or cable ties to facilitate the sealing if needed.
- Fill a large bucket with water. Submerge the valve and the gas inlet-tube connection under water.
- Turn on the gas sampling device.
- The dissolved gas in the groundwater is then stripped from the water and pumped out through the gas outlet of the gas extraction device.
- The design of the valve on the sampling gas bag ensures that it does not block the sampling pump, which would cause an abrupt influx of air when the valve is opened. When the valve is shut, the sample flows down the valve stem and exits via a small outlet hole located above the valve. (See Fig. 2b). Bubbles should be seen coming out of this exhaust under water. Let the gas flow for around 10 seconds (if needed) so that all the air inside the tubing is flushed out.



FIG. 2. Sampling Bag Validated for Field Gas Sampling for ATTA Analysis

- Open the valve so that the flow is directed into the bag.
- Fill the bag to a capacity of 50 to 60% and then close the valve. Do NOT fill the bag to its full volume. Leave some room for the gas to expand when it is shipped via an airplane.
- Close the valve when the sampling is finished.

NOTE: it is advised that sampling bags should not be reused.

2.3. ADDITIONAL NOTES

Concentrations of ^{81}Kr will be reported relative to the concentration in modern air. Concentration of ^{85}Kr is given for all samples in dpm/cm³ (decays per minute per cm³STP of krypton) and is calibrated against the low-level counting laboratory at the University of Bern. Blind duplicate samples and intra-lab comparison (e.g., USTC vs. ANL) are recommended, one for each sampling campaign. General description of the data handling and data reduction is given in Section 6 of this volume.

The descriptions and instructions for ^{81}Kr dating provided in this section should be viewed as a general guideline. For special cases, unconventional sampling methods may be possible. The research team should consult with the laboratories with sampling expertise. ^{39}Ar dating is also available with limited capacities as the throughput for ^{39}Ar in the ATTA labs is still lower than ^{81}Kr . The research team should make inquiries with the ATTA labs that capable of measuring ^{39}Ar .

3. SELECTION OF SAMPLING SITE FOR ^{81}Kr AGE DATING BASED ON ^4He CONCENTRATION

ATTA analysis is a powerful tool for groundwater age determination. However, it requires specialized equipment for sampling [28-30], and a certain level of training. Furthermore, the preparation of gas samples for analysis requires a purpose-built gas purification system [28, 31-33], making it considerably more challenging compared to stable noble gas analysis. Therefore, before attempting ^{81}Kr dating on groundwater, it is crucial to conduct a preliminary investigation to determine whether the groundwater of interest falls within the applicable range of the ^{81}Kr method. In this section, we discuss a method that utilizes ^4He as an indicator for screening the age of groundwater in wells, ensuring that the efforts in the field to collect samples for ^{81}Kr analysis are not in vain.

3.1. ^4He AS A GROUNDWATER AGE PROXY

The concentration of ^4He in groundwater is a valuable tracer for estimating groundwater residence time [34]. ^4He is a stable isotope primarily produced through the radioactive decay of uranium and thorium in the Earth's crust. When groundwater infiltrates into the subsurface, it interacts with rocks and minerals, leading to the release and dissolution of ^4He . As groundwater remains within the aquifer system, the concentration of ^4He gradually increases. The presence of ^4He from underlying reservoirs, known as "terrigenic" helium, can serve as a qualitative or semi-quantitative age proxy [35-37] when the accumulation rate of the terrigenic component is known.

Based on Fig. 3, the analysis of ^4He concentrations in groundwater samples from 11 distinct aquifers targeted in the CRP demonstrated a wide range of concentrations, ranging from approximately $(3 \sim 5) \times 10^{-8} \text{ cm}^3\text{STP/g}$ to $1 \times 10^{-3} \text{ cm}^3\text{STP/g}$. Groundwater samples with ^4He concentrations around the order of $10^{-8} \text{ cm}^3\text{STP/g}$ suggest recent recharge, as they align closely with the expected equilibrium solubility of ^4He in water at atmospheric pressure (ASW). Notably, these samples showed no indications of Terrigenic ^4He accumulation. Conversely, most samples exhibited ^4He concentrations exceeding $10^{-7} \text{ cm}^3\text{STP/g}$, indicating the accumulation of Terrigenic ^4He over extended time periods.

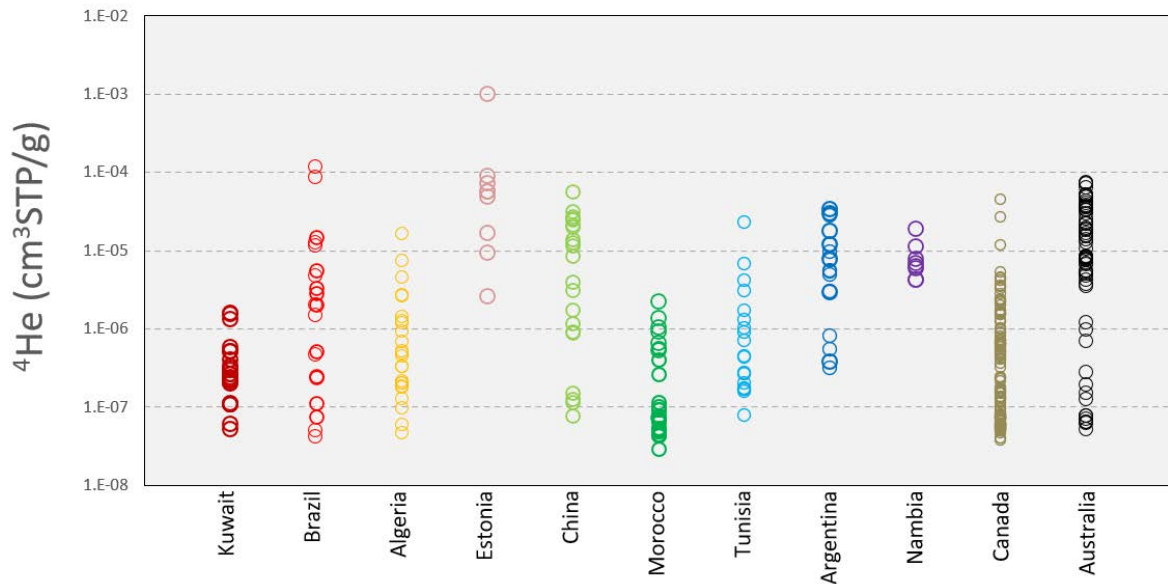


FIG. 3. Concentration of ^4He in groundwater from the CRP projects.

3.2. SOURCE OF THE TERRIGENIC HELIUM COMPONENT

The source(s) of Terrigenic helium can be identified by using a three-isotope diagram with potential endmember components (i.e., the mantle- and the crustal (radiogenic)-helium components). As shown in Fig. 4 where ratios of $^3\text{He}/^4\text{He}$ and Ne/He from the case studies in the CRP are plotted, most of the data are consistent with the three-component mixing among two distinct terrigenic components (the mantle-He and the crustal-He) and the atmospheric helium acquired upon groundwater recharge.

The data shows distinct distributions for each groundwater system. For example, samples from Brazil (the Guarani Aquifer [38], exhibit a clear trend along a mixing line from atmospheric endmember to the continental crustal component. As their groundwater ages become older, they align closer to the continental crustal endmember, consistent with the expected increase in the concentration of radiogenic ^4He with age (= lower He/Ne ratios).

It is also notable that there are some suites of samples showing systematic departure from the air-crust mixing line, namely those from Morocco, Canada and China. One crucial aspect to highlight in the context of groundwater age dating is the significance of mantle-derived helium. The $^3\text{He}/^4\text{He}$ ratio of the mantle endmember is approximately 1000 times higher than the radiogenic $^3\text{He}/^4\text{He}$ ratios found in the crust. Local tectonic activity can introduce helium from the mantle. Fossil mantle signal could also occur in groundwater which is acquired during water-rock interactions [39]. However, note that contribution of the mantle component has minimal effect on the ^4He concentrations. This is exemplified by the findings of Matsumoto et al. [40], where certain samples clearly exhibited indications of the mantle-derived component, as depicted in Fig. 4. The study concluded that, even with the obvious contribution of the mantle-derived helium, over 95% of the ^4He can be attributed to the terrigenic component originating from the continental crust.

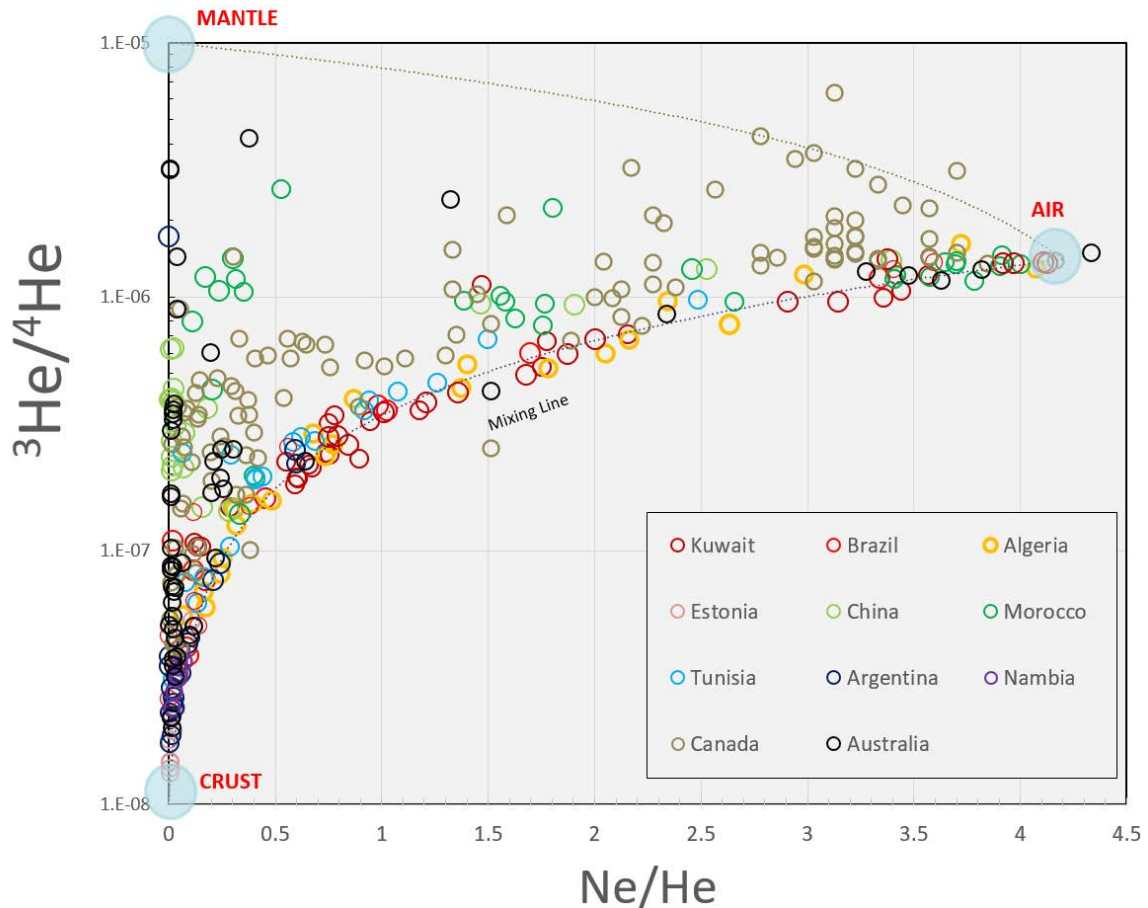


FIG. 4. Three-isotope-diagram of ^3He , ^4He and Ne . Two curves represent binary mixing trends between an atmospheric component dissolved in water and the mantle and the crustal components. Data collected during the CRP.

3.3. EXPLORING THE POTENTIAL AGE RANGE INFERRED FROM ^4He

In this section, we investigate the possibility of using ^4He to identify suitable radioactive age tracers when appropriate tracers are challenging to employ in groundwater analysis.

Figure 5a presents the ^4He concentration versus ^{14}C ages from the CRP projects. A gradual positive correlation between helium concentration in groundwater and radiocarbon ages is observed and is consistent with the expected time-dependent increase in ^4He concentration. However, this trend disappears for samples with groundwater ages greater than about 10,000 years. Beyond this range, even in samples with extremely high ^4He concentrations, radiocarbon ages converge to several hundred thousand years. This phenomenon arises due to the inherent limitations of the radiocarbon dating method, which is reliable only up to 20,000 to 30,000 years and does not accurately represent the distribution of actual age values.

In contrast, the comparison of age values determined using ^{81}Kr within the same sample set reveals that the actual ages surpass the limitations of radiocarbon dating and are significantly older (see Fig. 5b). Notably, when ^{14}C ages exceed 10,000 years but exhibit ^4He concentrations greater than $10^{-6} \text{ cm}^3\text{STP/g}$, it becomes reasonable to assume that these ^{14}C ages do not reflect

the actual ages accurately. This underscores the significance of employing suitable age tracers to ensure precise determination of groundwater ages. Empirically derived knowledge regarding the applicability of age tracers and groundwater ages serves as valuable criteria for selecting appropriate age tracers based on ^4He concentrations. (Table 1).

TABLE 1. AGE RANGES, HELIUM CONCENTRATION, AND AGE TRACERS FOR GROUNDWATER AGE DATING

| Age Range (yrs) | Helium concentration ($\text{cm}^3\text{STP/g}$) | Age Tracers |
|-----------------|---|---|
| 0-60 | $< 10^{-7}$ | T- ^3He , ^{85}Kr , SF_6 & CFC |
| 60-10,000 | $10^{-7} - 10^{-6}$ | ^{39}Ar , ^{14}C |
| 50,000-100,000 | $> 10^{-6}$ | ^{81}Kr , ^{36}Cl |
| $> \sim 1,000$ | $> 10^{-7} \sim -6$ | ^4He |

In Table 1, ^4He is listed as an age tracer. However, it should be noted that the ^4He age dating method differs from those using radioactive isotope decay (such as T- ^3He , ^{39}Ar , ^{14}C , ^{81}Kr , and ^{36}Cl) or time-series input functions (like Tritium, ^{85}Kr , SF_6 and Chlorofluorocarbon (CFC)). The ^4He method requires knowledge or assumptions about the rates at which radiogenic ^4He from crustal basement rock or the mantle transfers and accumulates in groundwater, as well as constraints on the *in situ* production of radiogenic ^4He in the aquifer matrix. Several models have been proposed to determine ages based on ^4He concentrations (e.g., [16, 26, 41-45]).

There are a few case studies from the CRP that successfully estimated the ^4He (model) ages by using ^{81}Kr ages to calibrate the ^4He transfer model within an aquifer [16, 26, 45, 46]. This highlights the usefulness of combining age tracers that complement each other. Groundwater sampling and analysis for the ^4He method are relatively straightforward and rapid compared to those for the ^{81}Kr age dating. The ^{81}Kr analysis by ATTA is currently limited to a few facilities worldwide, with limited throughput per instrument per year. Besides, the sampling for the ATTA ^{81}Kr analysis requires the purpose-built sampling device and subsequent laboratory processing to purify a few micro litre of krypton from the gases dissolved in groundwater samples (Sections 5 and 6).

Furthermore, as demonstrated in this section, it is possible to select suitable age tracers by utilizing helium concentrations. The use of portable mass spectrometers (gas-equilibrium-inlet mass spectrometer, GE-MIMS), which have been developed in recent years, could make helium-based filtering at sampling sites even more convenient. The device shown in Fig. 6 (miniRuedi, Gasometrix) allows for the direct extraction of dissolved gases from groundwater using a membrane filter and subsequent mass spectrometry analysis [47]. Since helium-4 can also be quantified with this device, it becomes feasible to determine the appropriate absolute age tracer on-site using the criteria presented in Table 1. It should be noted that this device cannot analyze the helium isotopic ratio ($^3\text{He}/^4\text{He}$) and its quantification accuracy is not as high

as that of traditional high-performance mass spectrometers. Therefore, it remains important to collect samples for laboratory analysis using conventional methods as necessary for data interpretation and estimating the ^4He ages.

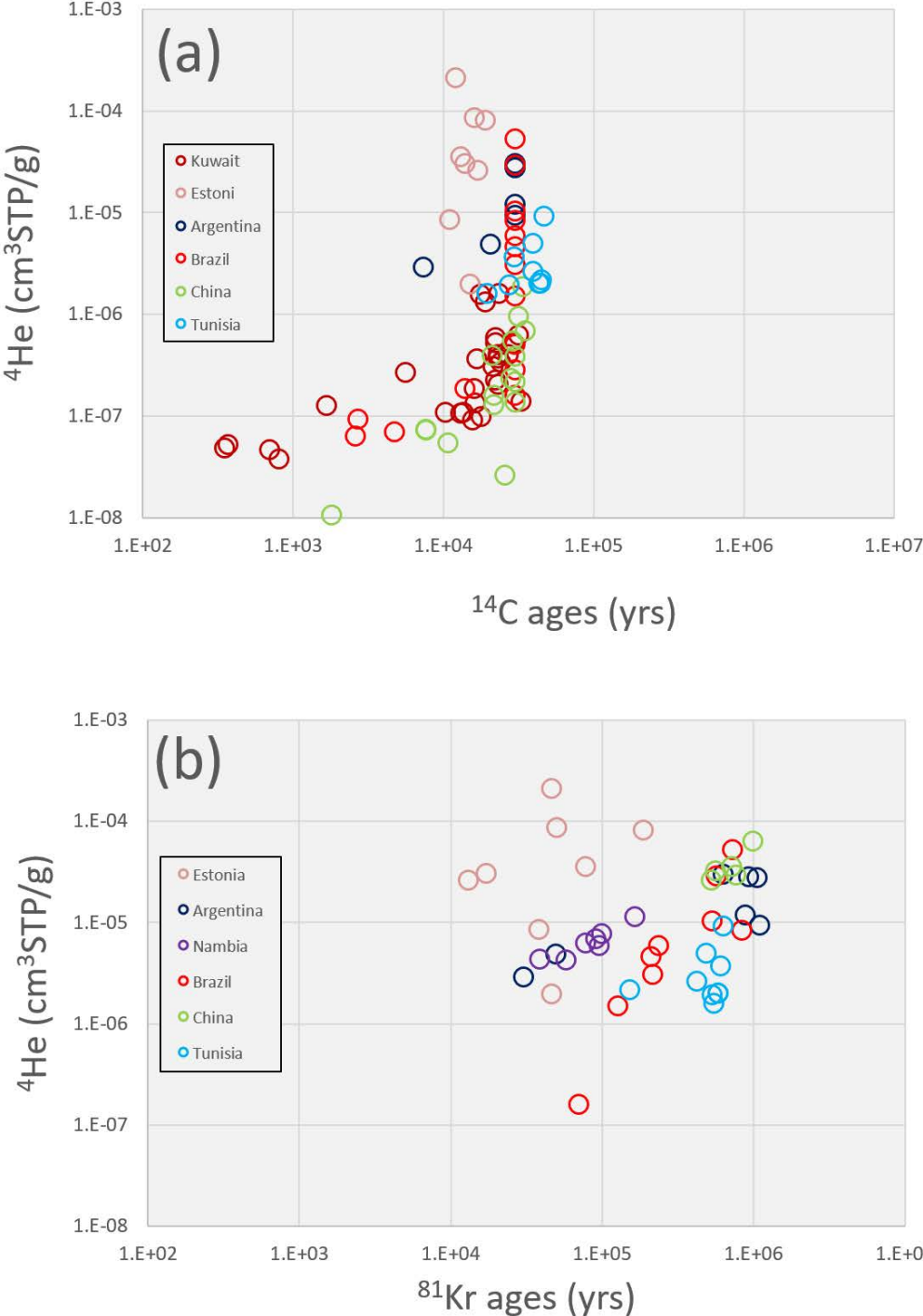


FIG. 5. ^4He abundance and (a) ^{14}C ages and (b) ^{81}Kr ages measured for the CRP projects.



FIG. 6. Portable mass spectrometer system (miniRuedi, Gasometrix) being used in the field to analyze dissolved gases including ^4He .

4. SAMPLING METHODOLOGY FOR GROUNDWATER AGE DATING WITH ⁸¹Kr

This section will serve as an in-depth guide to the setup and operation of sampling devices available from the IHL, IAEA, for Member States' projects. As highlighted, radioactive krypton isotopes (⁸¹Kr and ⁸⁵Kr) are considered reliable tools for groundwater age determination. ⁸¹Kr originates from a cosmic ray-induced reaction in the atmosphere and possesses a half-life of 229,000 years. In contrast, ⁸⁵Kr, a byproduct of nuclear weapon detonation and uranium/plutonium fuel processing, has a half-life of 10.8 years. These isotopes cater to the dating of both ancient (spanning 50,000–2,000,000 years with ⁸¹Kr) and more recent (up to 100 years with ⁸⁵Kr) groundwater. Nonetheless, due to their notably low natural abundance, the volume of water necessary to extract ample krypton isotopes is substantial, exceeding 1 ton. To facilitate the in-field collection of dissolved gases in groundwater, the IHL adopted a gas sampler inspired by the design proposed by Mr. Neil Sturchio of the University of Illinois, Chicago [29]. This device can extract and concentrate gases from a continuous flow of water in the sampling field using a polyethylene membrane contactor. Currently, two sampling devices (IAEA-EDGAR-Mk I and IAEA-EDGAR-Mk II, EDGAR stands for Extraction of Dissolved Gases for Analysis of Radio-Krypton [29]) are available for Member States from the IHL, IAEA, and the standard operating procedures of both units are described here.

4.1. FIELD DEGASSING DEVICE

As previously mentioned, advancements in ATTA render radio-krypton analysis a viable option for determining groundwater age. Yet, despite the enhanced isotope sensitivity offered by ATTA, the inherently low presence of krypton in the air (the main contributor to krypton dissolved in groundwater) requires approximately 100 L of water to yield adequate krypton volumes for the analysis. Therefore, for age dating using radio-krypton isotopes, dissolved gases have to be extracted and collected on-site, as exemplified in references such as [33].

The sampling devices used by the IHL are detailed in [28], and a schematic representation can be found in Fig. 7. These devices primarily feature a hydrophobic semi-permeable hollow fiber membrane contactor. This key component enables the extraction of dissolved gases from water as it flows through the contactor cartridge. The efficiency of gas extraction via the membrane contactor is highly dependent on the vacuum level on the gas side of the contactor [28]. As depicted in Fig. 8, the contactor's extraction efficiency reaches approximately 90% when the gas pressure is maintained at around 100 mbar. Furthermore, the contactor's extraction capacity is sufficiently large, leading to consistent extraction efficiency across different water flow rates, ranging from 5 to 15 L/min. Both versions of the IAEA's EDGARs are designed to keep the gas pressure below 200 mbar, which ensures a high level of extraction of dissolved gases. In these systems, the time required for collecting the targeted gas volume is primarily dependent on the water flow rate available in the field, as noted in [28]. It is important to mention that these samplers have been utilized in various sampling campaigns in past IAEA research projects, as referenced in [16, 26, 45].

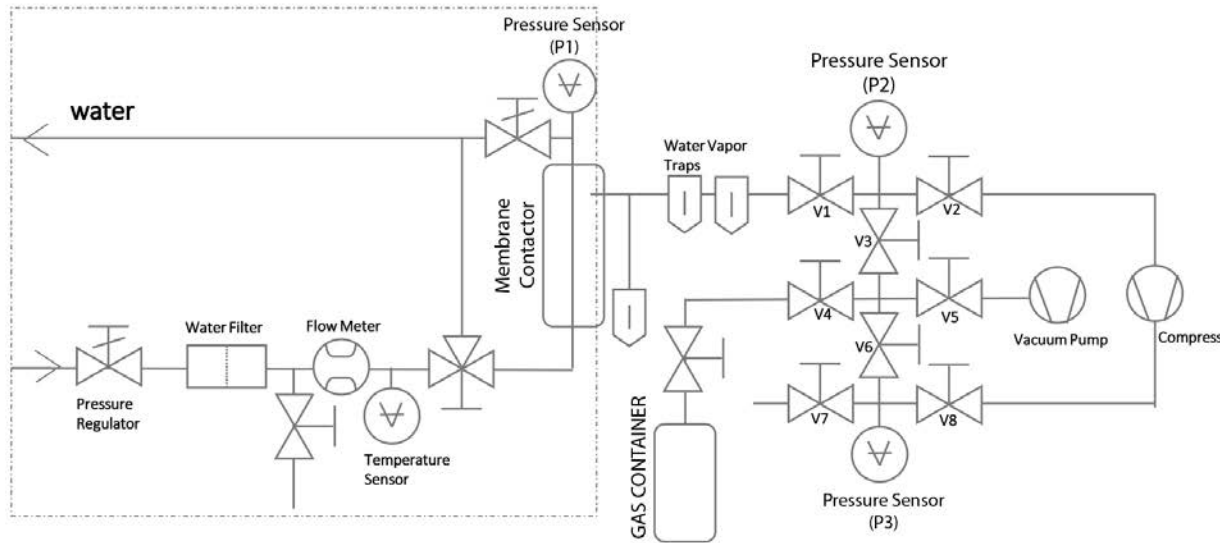


FIG. 7. A schematic illustrating the IAEA's field gas sampler used for radiokrypton analysis, known as the IAEA EDGAR-Mk-I. For the Mk-II version, the use of a vacuum pump is optional.

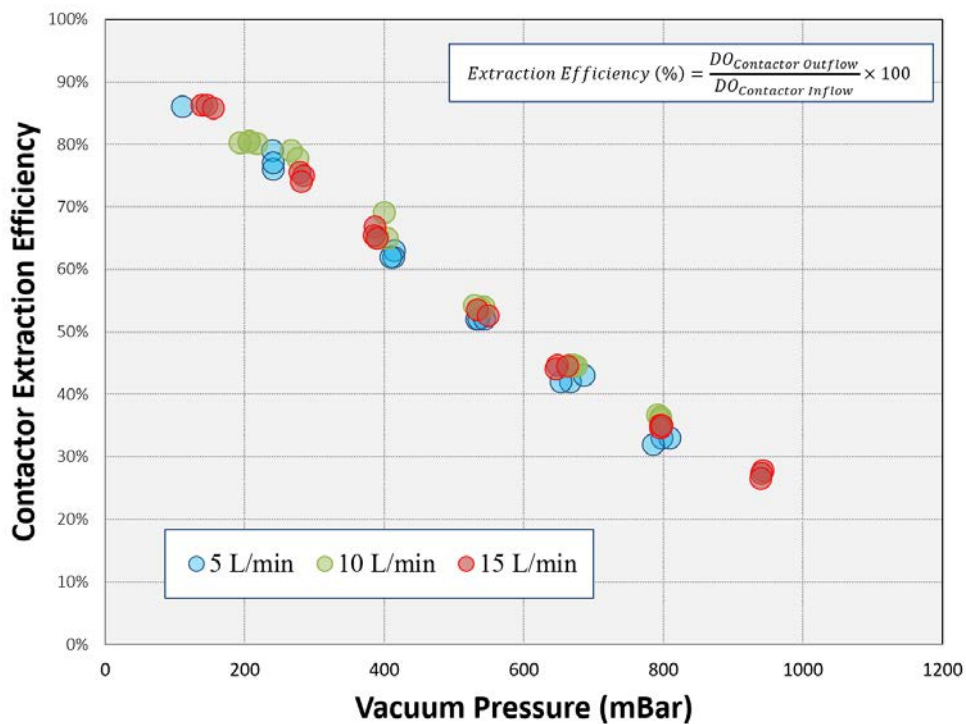


FIG. 8. The performance of the IAEA-EDGAR Mk-I membrane contactor, as measured by Dissolved Oxygen (DO) levels before and after the process, relative to vacuum pressures on the contactor's external surface, across three distinct water flow rates. Reproduced from [28] with permission from Elsevier.

The original model, referred to as IAEA-EDGAR-Mk I, was designed with the primary objective of collecting 40 liters of dissolved gases in the field within a few hours. To achieve this, the device was equipped with a sizeable contactor cartridge and two pump units, with one serving as a compressor and the other utilized for evacuating a sample canister. Consequently, this first-generation device boasted dimensions of $104 \times 52 \times 34$ cm and weighed a substantial 80 kilograms. Over the past decade, significant advancements have been made in improving ATTA's detection limits for radio-krypton analysis (see Section 2). Consequently, the current requirement for the volume of extracted gas has been reduced to a range of 5 to 10 liters. As a result, gas sampling can now be accomplished using specialized sampling bags, such as the Supel™-Inert Multi-Layer Foil, while maintaining the internal gas pressure at atmospheric levels. This eliminates the need to collect 40 liters of gas in pressurized canisters, a requirement driven by considerations of size and transport logistics.

The utilization of sampling bags, as opposed to canisters, has the added benefit of simplifying the sampling procedure. Unused sampling bags do not contain any gases, eliminating the need for field evacuation and purging, and obviating the necessity for an additional vacuum pump alongside the compressor. Furthermore, the reduced gas volume requirement allows for the adoption of a smaller contactor cartridge. These factors collectively contribute to a significant reduction in the size of the second-generation sampler, known as IAEA-EDGAR-Mk II, which now weighs 41 kilograms and measures $60 \times 50 \times 32$ cm in dimensions. It's important to note that the smaller contactor cartridge in the second-generation device results in a lower surface area for the water/gas interface, which translates to an overall extraction speed approximately 40% slower compared to the first-generation machine. However, this reduced extraction speed is well-compensated by the smaller sample size now required to achieve the desired sensitivity levels for ATTA.

To ensure the integrity of the system, leak rates were meticulously assessed by operating the samplers with the contactor cartridges filled with degassed water and quantifying the amount of gas collected at the compressor exit port. These evaluations confirmed that the leak rates were less than 20 cm³ in one hour of operation, constituting less than 0.1% of the krypton content typically present in a standard 10-liter sample of gas, rendering them negligible.

4.2. STANDARD OPERATING PROCEDURE OF IAEA-EDGAR-MK I

The purpose of this section is to describe the configuration and detailed operating procedures of the IAEA-EDGAR-MK I used in the sampling campaign supported by IHL (Fig. 9). The IHL provides this sampling device along with all the necessary tools for the field, such as various sizes of pipe adapters.

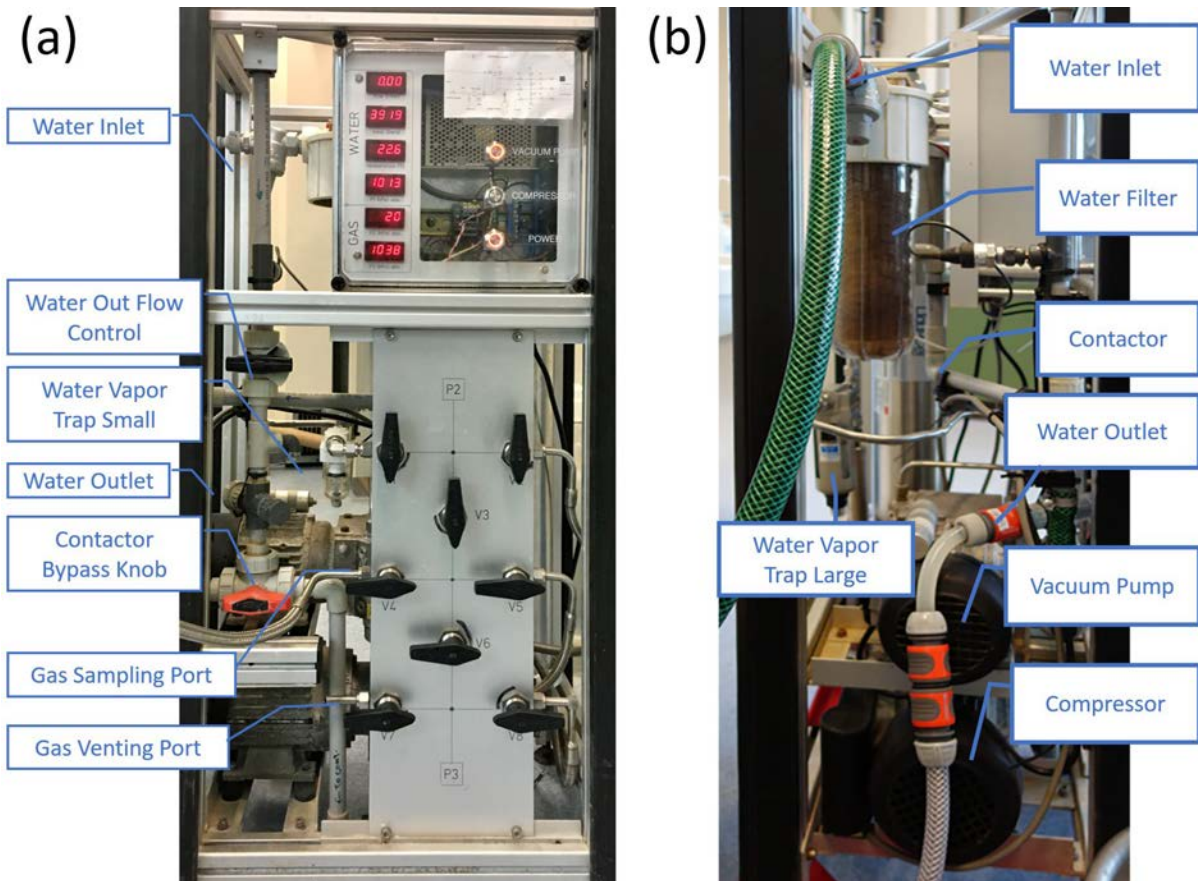


FIG. 9. Overview of the IAEA-EDGAR-MK I (front and side view).

The following is a comprehensive set of instructions for conducting field sampling.

4.2.1. Water Flow Connection

To establish a leak-free connection between the sampling device and the sampling outlet, users are advised to follow the steps outlined below, which entail connecting a hose through the sampling device from the wellhead at the sampling site to the point of discharge. Following is the instructions which are intended to ensure that the sampling process is carried out in a consistent and reliable manner, and that the integrity of the sample is not compromised.

- Establish a water hose connection from the well's water outlet to the sampler via water distributor (Fig. 10).

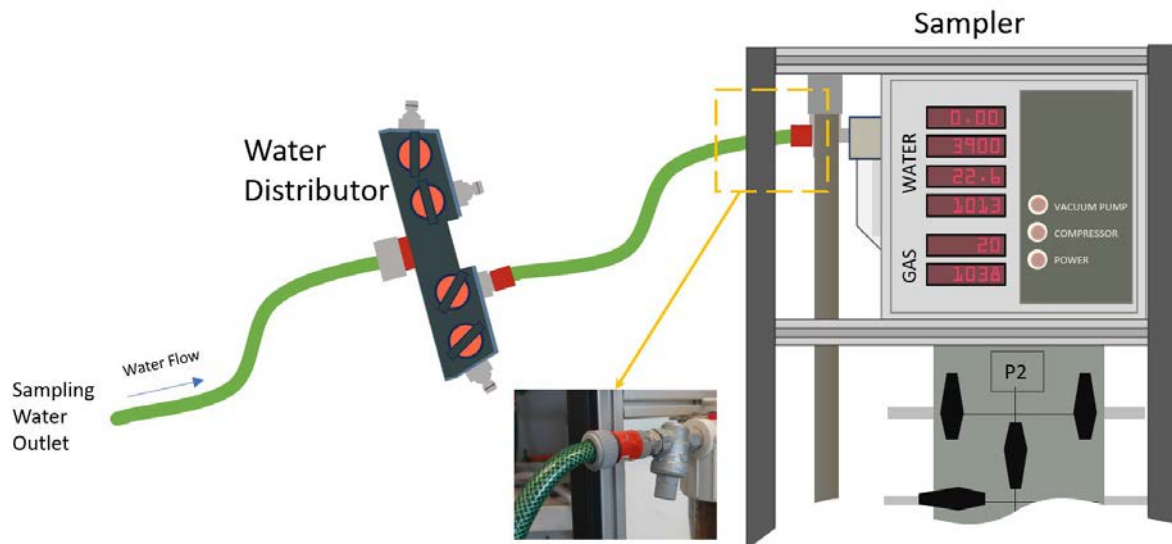


FIG. 10. Connection of water hoses from the sampling outlet to the water inlet port of the sampling device.

- Connect the drain tube to the Water Outlet port of the sampler (Fig.11). The other end of the drain tube should be placed somewhere appropriate (not to wet the device with the drained water).



FIG. 11. Connection of water hose from the water outlet port

- Make sure the bottom flange at the contactor is also tightly closed with the designated rubber O-ring and a clamp (Fig. 12).

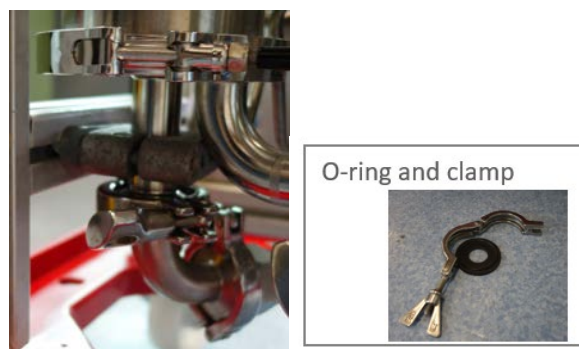


FIG. 12. Close-up view of the connection at the contactor casing and the O-ring and clamp.

- Make sure that water filter’s case is placed and closed tight (check by grabbing the transparent case and twist it to the direction shown in the picture) (Fig. 13).



FIG. 13. Water filter casing with an arrow indicating the direction of the turn to close it.

- Connect the power cable to the sampler, and press “Power (Fig. 14)” (Do not start the pump and compressor yet)

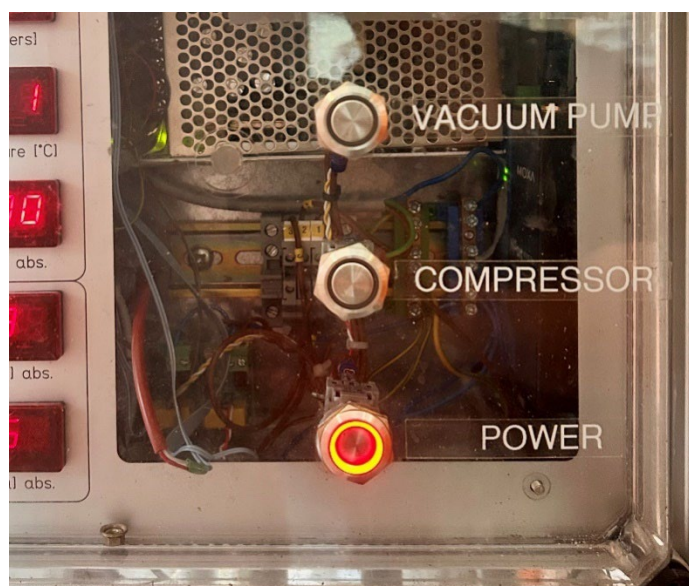


FIG. 14. Front panel of the device showing the 'POWER' button.

- Close the distributor’s port to the sampler and open rest of the ports. Start running the water. Check the temperature using a probe.
- Open the valve at the distributor (to the sampler) slowly, while monitoring “Flow”, “Temperature” and “P1 (water pressure)”. Do not let 100% of water flow directly to the sampler from the beginning – too much water pressure may damage the contactor. Use the distributor outlets to reduce/control the flow to the sampler. Water flow rate of 10-20 L/min is good for sampling. (# sampling with lower flow rates is possible, but it will take longer time).

The presence of bubbles can be problematic and may have a significant impact on the final isotopic analysis results in certain cases. Therefore, it is important to verify the absence of bubbles after establishing the water flow in the field, using the methods and criteria listed below for confirmation.

- If there are bubbles at water tube connection, outside air might be being sucked in by the water flow. To prevent the sample from being contaminated by air bubbles, the opening should be located and closed promptly.
- If bubbles are still visible in the water filter or the water tubes after removing any possible leaks, it is possible that these bubbles are the result of gas exsolution from the water during decompression of gas-rich water. In such cases, these bubbles should be considered as part of the sample that needs to be collected. At this stage, there is no effective way to control or prevent the formation of such bubbles, and it is generally not necessary to do so.
- It is important to ensure that the sampling equipment and procedures are designed to minimize any potential contamination of the sample by external sources. If uncertainty exists regarding the origin of bubbles, increasing the back pressure of the water by slightly closing the water outflow control valve may help to clarify whether the bubbles are due to water-related factors or leaks. If the number of bubbles decreases under these conditions, it suggests that the bubbles are derived from the water and not associated with any leaks in the sampling system.

4.2.2. Gas Flow Connection

As previously mentioned, gases separated on the contactor surface are transported through gas-specific manifold that is independent of the water flow path and are ultimately collected in the sampling container. The flow of gases is primarily controlled by the opening and closing of valves.

There are eight valves at front panel which are to control gas flows. The valve is closed when the knob is in a vertical position relative to the direction of the pipeline. Conversely, the valve is open when the direction of the knob aligns with that of the pipeline. In an example below

Unlike the flow of water, the flow of gas cannot be visually confirmed. Therefore, it is important to carefully operate the valves after thoroughly understanding the device configuration. It is also important to note that before the following steps, look at the connecting part(s) for any dust/s grains, and remove them if present.

4.2.2.1. Connecting Sample Cylinder with Flexible Metal Tube

Connect the gas sampling canister to the equipment and tighten its valve counterclockwise (Fig. 15). Use caution, as this is different from the standard valve tightening method. Use Teflon gaskets for the flexible tubing within the equipment. After manually tightening, use a wrench to turn the valve an eighth of a turn for a secure closure.

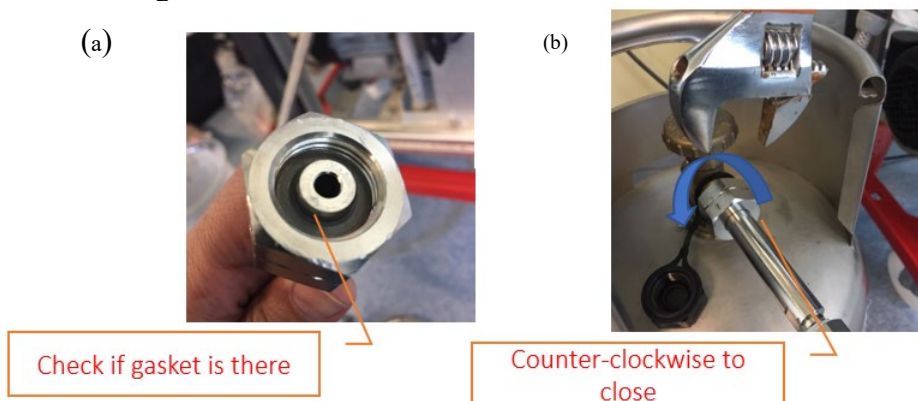


FIG. 15. (a) A view showing the Teflon gasket at the connection point from the sampler to the sampling canister, and (b) how to establish the connection.

4.2.2.2. Connecting Water Vapour Traps

Water vapor can enter the gas path through the contactor. However, condensed water can affect the efficiency of the pump or compressor, potentially causing problems with sampling. Therefore, sampling devices use multi-stage water vapor traps to remove water vapor from the sample gas. The following are the connection/check-up steps for the water vapor traps.

- Water Vapor Trap Small (Fig. 16): This water trap is equipped with a water release valve located at its bottom. To prevent air contamination, it is crucial to ensure that this valve is closed properly. To check that the bottom screw knob is securely closed, gently turn it clockwise until it feels tight. Take care not to apply excessive force as this component is delicate. If the knob feels tight, it is considered to be properly closed.



FIG. 16. Water vapour trap (small).

- Water Vapor Trap Large (Fig. 17): This water vapor trap can be detached by sliding down the black knob and giving it a 45-degree anti-clockwise turn (Fig.17(a)). Detaching the water vapour trap is achieved by sliding down the black knob and giving it a 45-degree anti-clockwise turn. The rubber gasket can be seen on the top left. When the trap is attached properly, a clicking sound can be heard, and the black knob is locked in, as shown in (FIG 17(b)).

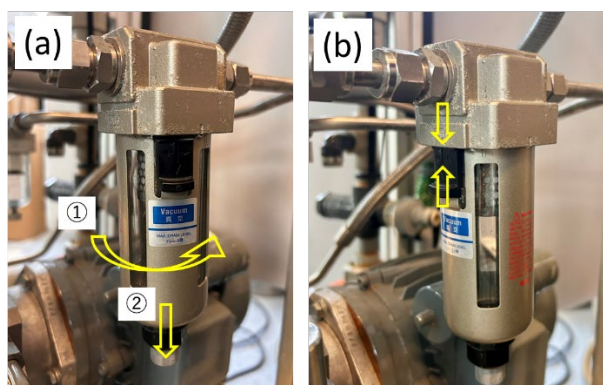


FIG. 17. (a) Large water vapor trap with arrows indicating the direction of movement for detaching the trap, and (b) the trap being properly attached with the black knob facing the flow direction and locked in.

4.2.2.3. Evacuating the Sample Container

Prior to sampling, it is necessary to evacuate the sample container. Any residual gas due to incomplete evacuation can mix with the sample, compromising the accuracy of the results. It is important to achieve a sufficient level of vacuum compared to the sample volume. After this step, the sample container will be adequately flushed with the sample gas, so as long as the procedure is followed correctly, the influence of residual gas should be completely eliminated.

- Set the valve conditions as shown below and open the valve at the sampling cylinder.

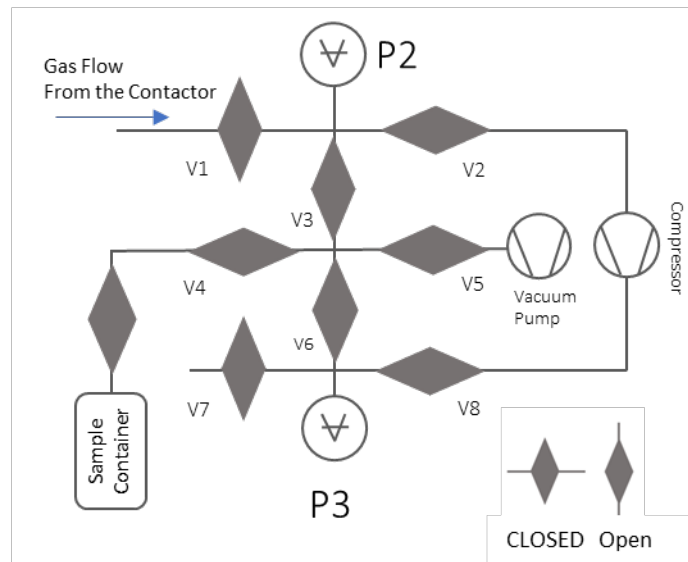


FIG. 18. Status of the valves during the initial evacuation of the system.

- Turn the main power on, and start the vacuum pump.
- The pressure readings P2 and P3 will drop rapidly during this step. Wait until both readings have stabilized and are low (P2 around 30 hPa and P3 around 50 hPa).
- Make sure to record the initial pressure readings for P2 and P3.

4.2.2.4. Leak Test

The gas flow path of the sampling device undergoes a rigorous leak test in the laboratory prior to shipment. However, there is still a possibility of leaks occurring during transportation due to vibrations and other factors. Therefore, a simple leak test should always be performed before starting the sampling process. The following are the steps for conducting the test.

- The leak test is conducted on a vacuum-purged system with the pump detached to verify its vacuum level. First, close valve V5 to separate most of the sampling system from the vacuum pump (Fig. 19). If there is a leak, the vacuum gauge reading should increase.

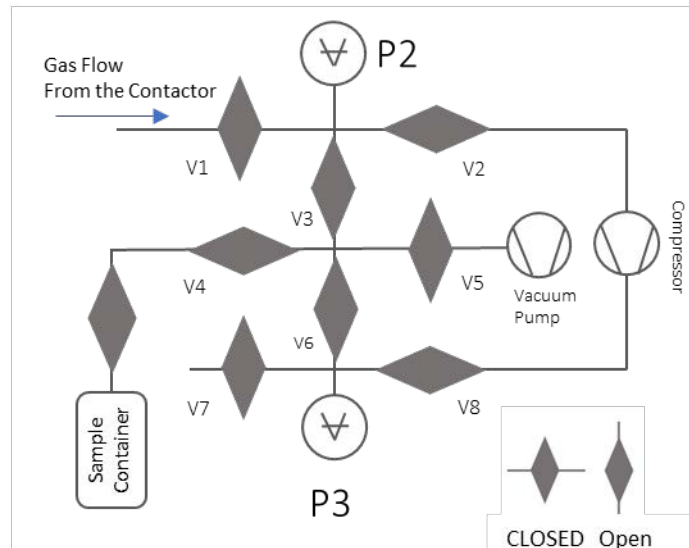


FIG. 19. Status of the valves before starting the leak test.

- Once P2 and P3 show no change for 2 minutes, it indicates that there is no leakage, and you can proceed to the next step in the section 'Turning on the Compressor'. If both P2 and P3 values increase during the leak test, it suggests a potential leak in the system, especially at the connections where the flexible tube attaches to the sample container. To identify the precise location of the leak, close V4 and observe whether the pressure increase subsides (Fig. 20). If the pressure increase stops, it indicates that the leak is likely located between V4 and the sample container (marked in a red shape in Fig. 20).

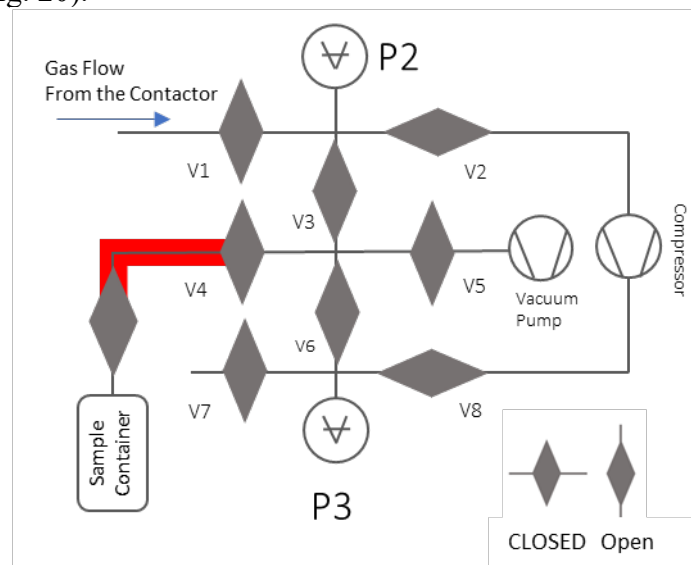


FIG. 20. Status of the valves to identify a leaky spot when P2 and P3 increase in the leak test.

- Attempt to slightly tighten the Swagelok connection at V4 and the cylinder connections in the counter-clockwise direction. Subsequently, reopen V4 and V5, and repeat the process of conducting a leak check.

- Close V4 and V5. If P2 and P3 readings continue to rise, establish the base pressure by opening V5 while keeping V4 closed. Next, isolate the compressor from the rest of the system by closing V2, V5, and V8. If the pressure increase ceases, it suggests a possible leak between V2 and V8 (indicated in red in Fig. 21), which includes the compressor, or the presence of moisture within the compressor.

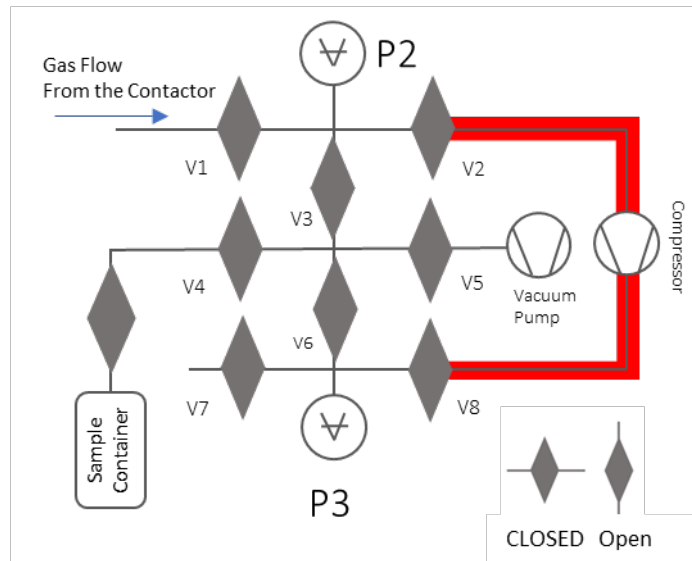


FIG. 21. Status of the valves to identify a leaky spot when P2 and P3 increase in the leak test.

- Open V5 to decrease P2 and P3 levels once again. Wait until reaching the lowest achievable pressure. Close V5 and then close V3 (Fig. 22). If P2 increases, it indicates a leak in the area between V1, V3, and V2 (referred to as area 1 in Fig. 22). If P3 increases, attempt to close V6. If P3 ceases to rise when V6 is closed, then the leak is located between V3, V4, V5, and V6 (area 2 of Fig. 22). If P3 continues to increase, the leak is likely situated somewhere between V6, V7, and V8 (area 3 of Fig. 22).

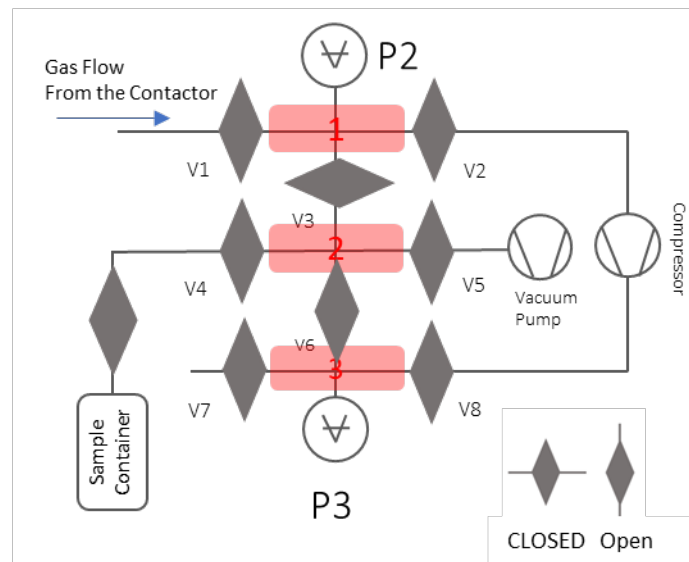


FIG. 22. Status of the valves at the last stage of the leak test.

In the field, leaks are identified and located by checking for changes in the vacuum level. As loose pipe connections are often the cause of leaks, once the location is identified, torque is carefully applied using an appropriate tool of the right size. After that, a leak test is performed to confirm whether the issue has been resolved. If pressure continues to rise, it's possible that

there is moisture inside the device. In this case, refer to the device drying procedure described below.

4.2.3. Gas Sampling Procedure

After completing the leak test, operate the compressor again. The system is flushed with sample gas by running the compressor and allowing the gas to flow through the system, and the sampling container is purged with the sample gas. Once the purging is complete, actual gas sampling can take place.

4.2.3.1. Turning On Compressor

- After completing the leak check, set the valves as shown in Fig. 23.
- Keep the pump running and continue pumping down the sample container.
- Start the compressor by pressing the button on the front panel.
- P2 should be under vacuum and at 50-60 hPa (if the system is dry). P3 should stay at atmospheric pressure (~1000 hPa).

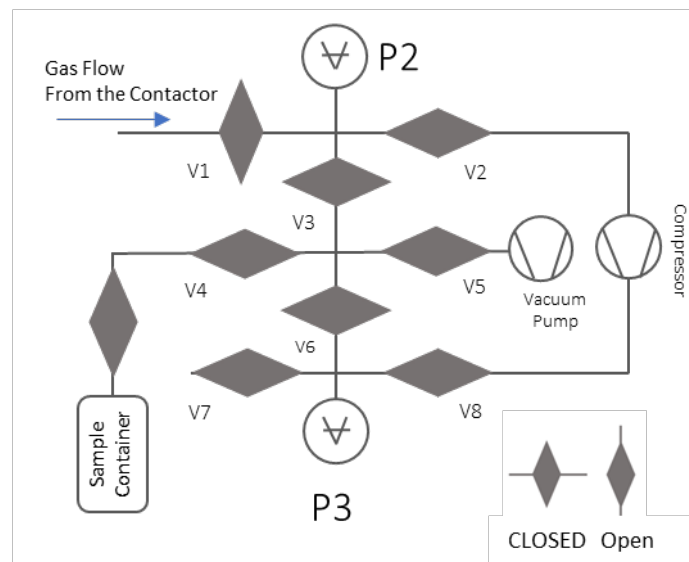


FIG. 23. Status of the valves for initial pumping down of the sample container and for starting the compressor.

- Close V2 and open V3.
- P2 should give the pressure reading inside the sample container. This process is just to check that the cylinder is empty (< 50 hPa).
- Close V3 and open V2.
- Prepare a water container (such as a water bucket) filled with the sampling water.
- Connect the transparent tube to the gas exhaust port (at V7) with a hose clamp (Fig. 24(a)).
- Confirm that P3 is showing atmospheric pressure.
- Put the other end of the transparent tube into the water (Fig. 24(b)).

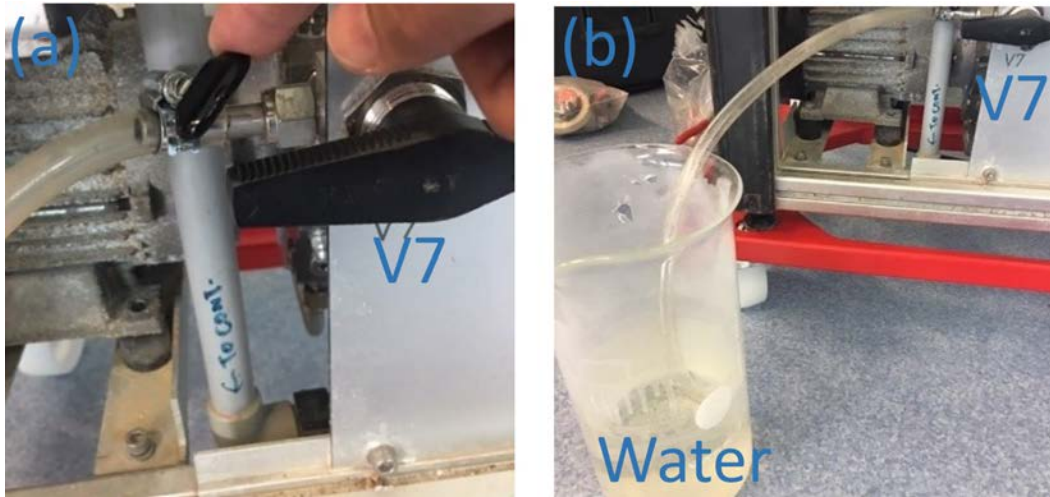


FIG. 24. Connection of the transparent tube to the gas exhaust at the V7, with (a) showing the hose clamp used to secure the connection, and (b) showing the tube submerged in water. The tube should always remain underwater until the V7 is closed for gas sampling.

4.2.3.2. Flushing

Keep an eye on P2, and also monitor the water level in two vapor traps.

- Open V1 slowly, and be prepared for intense bubbling at the gas exhaust water reservoir.
- Move the valve as little as possible to keep P2 below 200 hPa.
- If sampling from high temperature water, ensure the two water vapor traps are not completely filled. If the water is accumulating too quickly, close V1 and suspend sampling until the water temperature can be lowered or another site can be selected.
- After opening V1 fully, allow the system to fill with the gas sample for 10 minutes.
- During this time, observe bubbles in the water reservoir, which indicate the presence of the gas sample.

4.2.3.3. Purging

To purge the gas container with the sample gas, switch the valve from the exhaust position (Fig.25(a)) to the gas collection position, letting the gas flow into the sample container (Fig. 25(b)) following the steps below;

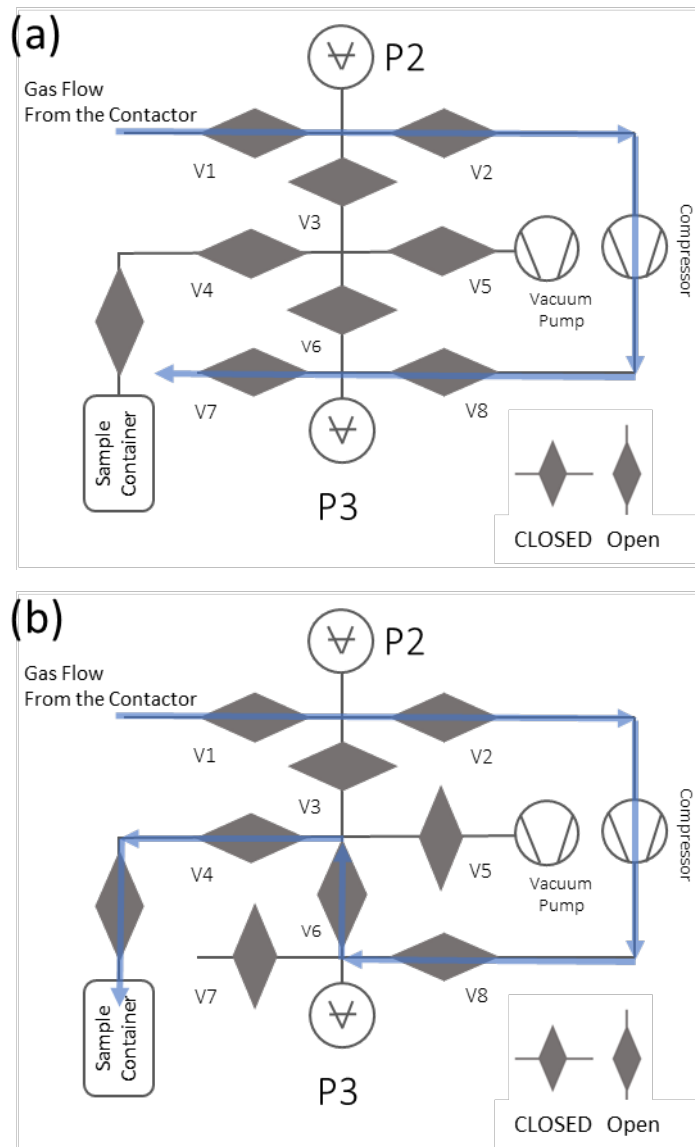


FIG. 25. (a) Status of the valves at the gas exhaust position, and (b) that at the gas sampling position.

- Close V5 (to isolate the pump)
- Close V7 (P3 started going up rapidly, but it is normal)
- Open quickly V6 (to let the gas samples flow into the sample container)
- Keep monitoring P2, P3, and always watch over the water levels in the vapor traps.
- P3 gives the pressure of the sample gas in the sample container.
- Wait until P3 reaches 20 times the initial empty volume pressure. (if the base pressure was 20 hPa, then wait until 400 hPa).
- Fold the transparent tube by one hand while the other end still well inside the water (to avoid the water flowing back into the compressor during the next step).
- Close V6, and Open V7. Then you immediately feel pressure developing inside the transparent tube (meaning P3 is higher than atmospheric). Unfold the tube and let it bubble in the water.
- Open V5 for 5 min.
- Check the pressure container by closing V1 and V2, and open V3.
- If P2 is low as an initial vacuum state, close V3, and open V2 and slowly V1.

- Repeat from step 1. (Purge at least twice to bring down the residual air $< 1/20000$ in the final collected sample).

4.2.3.4. Sample Gas Collection

It should be noted that during the collection process, P2 may gradually increase, which can slow down the rise of P3. Unfortunately, this cannot be rectified while sampling. At times, P2 may decrease again, while in other cases, it may remain high. If P2 remains high at 500 hPa, you may attempt to close V1 and monitor P2 for a drop before slowly reopening V1 to keep P2 low. However, if P3 is not rising, it's best to be patient and wait until the targeted pressure is achieved. Also note that the procedure to start sampling is the same as the “Purging” steps.

- Close V5 (to isolate the pump)
- Close V7 (P3 started going up rapidly, but it is normal)
- Quickly open V6 (to let the gas sample flow into the sample container)
- P3 going down again (by expansion to the larger volume)
- Keep monitoring P2, P3, and always watch over the water levels in the vapor traps.
- P3 gives the pressure of the sample gas in the sample container. It is necessary to wait until the target pressure is reached (minimum is 1200 hPa, but more gases can be collected if the sampling is extended).
- It is important to record P2 & P3 every 5 minutes.

When P3 reaches to the target pressure, proceed the following steps to finish sampling.

- Close the valve tightly at the sampling container (hand-tight).
- Record the final pressure (P3).
- Remove the transparent tube from the water reservoir and open V7.
- Remove the transparent tube from the exhaust port located at V7.
- Use a tool to give the valve at the sampling container extra torque (1/8 turn max).
- Put a sticky tape to seal the valve and write down the sample ID, date and time, and the final read out of the P3. This is to ensure that everyone in the team knows that the cylinder has a sample inside.
- Stop the water flow from the well to the sampler.
- Remove the water vapor trap tube (Fig. 26), which will break the vacuum and let air flow through the compressor to dry it up.

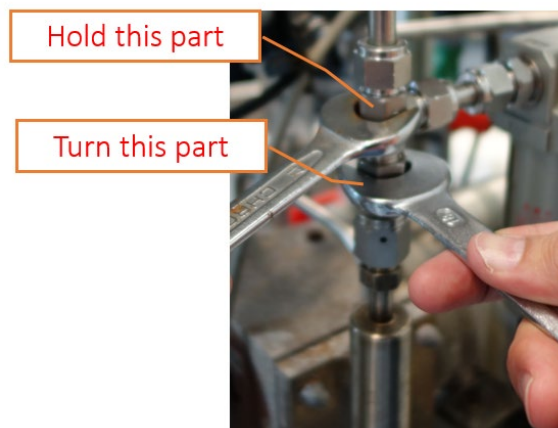


FIG. 26. Removing the water trap tube to vent the system.

- Close V6.

- Remove the metal flexible tube from the sampling cylinder and attach it to the sampler body with a cable-tie for transport.
- Open V5 to let air go through the vacuum pump.
- If there is water in the water vapor traps, remove or open the traps to remove water.
- Apply back pressure to enhance removal of water from the compressor by opening and closing V7 repeatedly or using your thumb to close the exhaust.
- Turn off the compressor, pump, and main, and then disconnect the power cable.
- Disconnect the water inlet tube from the sampler and cover the electrical parts of the sampler.
- Disconnect the water outlet tube from the sampler and cover the electrical parts of the sampler.
- Remove the water filter casing and empty it. If the water filter cartridge is dirty, rinse it to clean or replace it with a new one for the next sampling.
- Drain water from the contactor by opening the bottom flange at the contactor cartridge to remove water from it.
- Close all valves as in Fig. 27 and put the sampler into the transporting case.

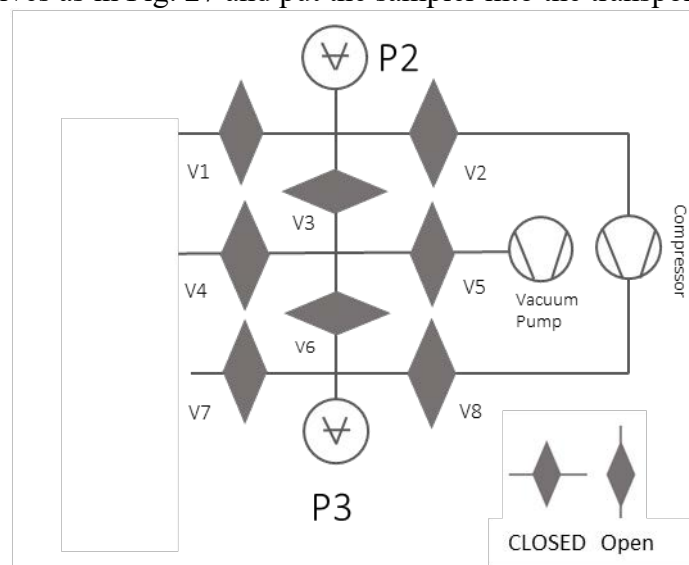


FIG. 27. Valve Status for storage and transportation

4.3. STANDARD OPERATING PROCEDURE OF IAEA-EDGAR-MK II

As mentioned earlier, the second iteration of IAEA-EDGAR was designed to enhance mobility in the field by reducing its dimensions and weight. EDGAR-MK II retains the same basic configuration as MK I, but the vacuum pump is now housed separately and can be connected in the field. Furthermore, by using a laptop PC to obtain pressure readings from the system, the electrical components have been significantly downsized (Fig. 28).

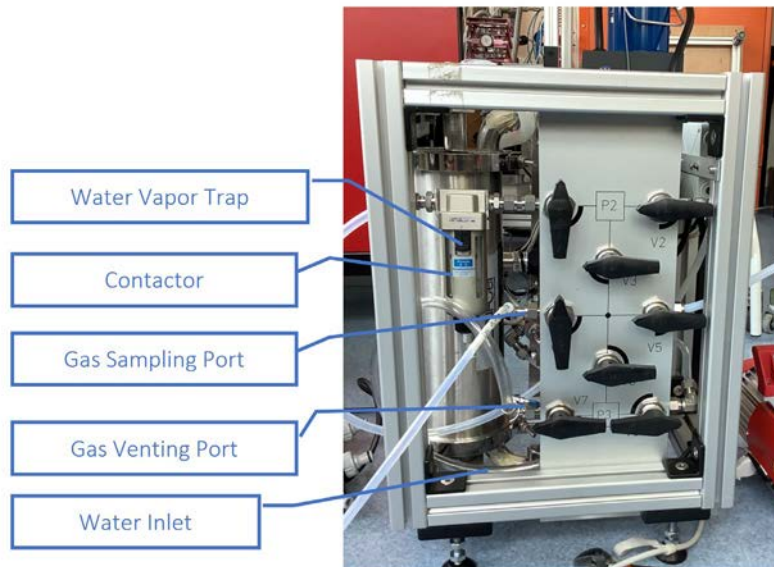


FIG. 28. IAEA-EDGAR-MK II. This sampler shares the same valve configuration as MK I

4.3.1. Preparation of the device

4.3.1.1. Water flow

These steps are described in order to show how to establish a water hose connection from the well's water outlet to the sampler (via water distributor). It is important to follow these steps before starting the water flow from the source.

- Connect the water distributor and Water Filter as shown Fig. 29.

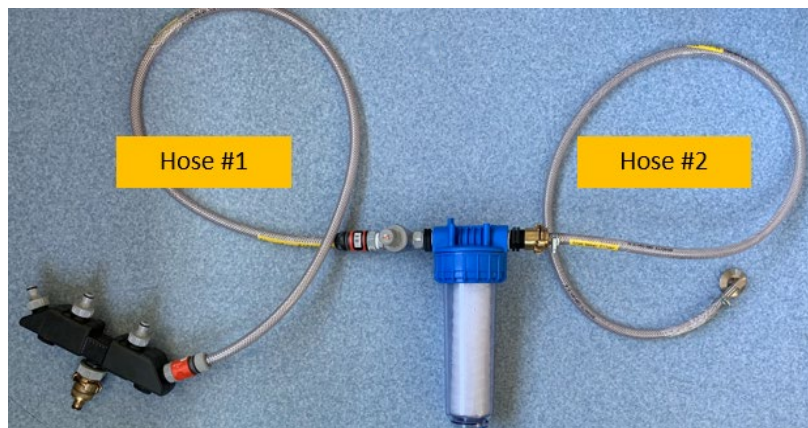


FIG. 29. Configuration of water hoses and filter connection to the sampler.

- Connect the end of Hose #2 to the Water Inlet of the sampler (refer to Fig. 28 and Fig. 30 for a close-up view). Ensure that the bottom flange at the water inlet is securely closed using the designated rubber O-ring and clamp.



FIG. 30. A picture showing the bottom flange and clamp at the sampler's water inlet port.

- Attach Hose #3 to the water outlet port of the sampler (refer to Fig. 28 and Fig. 31 for a close-up view) and connect the other end to a drainage area located away from the sampler.



FIG. 31. A picture showing the water outlet port and the connection to the Hose #3.

4.3.1.2. Connect an external vacuum pump

The MK-II system features an external vacuum pump in order to reduce its weight. While it is possible to conduct a sampling protocol without a vacuum pump using a sampling bag, this requires cumbersome valve operation in the field. Therefore, it is currently recommended to use the vacuum pump and follow the simpler procedure rather than the procedure without the vacuum pump.

- Put the vacuum pump on a flat surface. Connect the power cable to the power distributor.
- Connect the tube from V5 to the pump (hand tight plus 1/4 turn with 18 mm spanner).

4.3.1.3. Data logger setup

- Connect the data logger cables from the sampler to the data logger as indicated in Fig. 32.

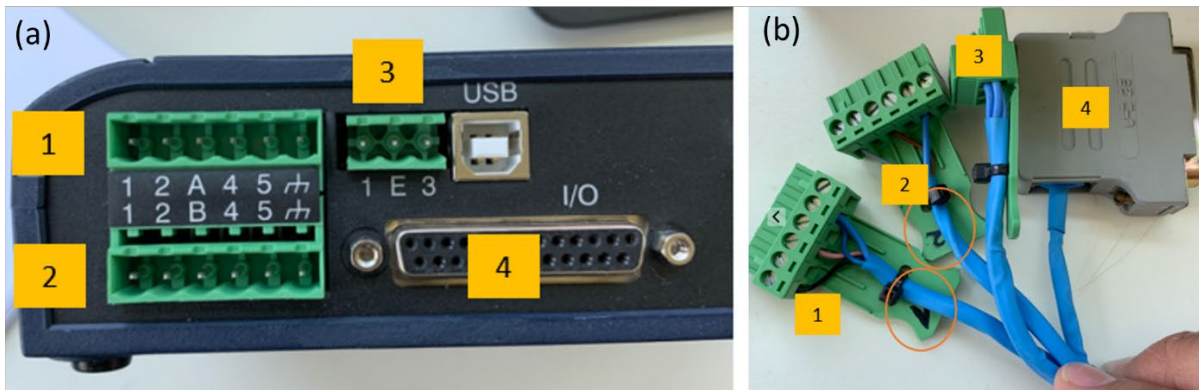


FIG. 32. (a) a picture showing the interface port on the back of the logger, (b) the data cable from the sampler. Ensure the cable is inserted into the port with the corresponding number.

- Connect the data logger to the laptop using a USB cable.
- Connect the power cables from the sampler, data logger, and laptop to a 240V AC power source.
- Power on the laptop and log in using the username "Krypton" and password "krypton" (all lowercase).
- Launch the logger software "Omegalog" located on the desktop. Navigate to "meter mode" to view sensor readings. Note that only pressure readings are accurate at this time, and temperature readings should not be relied upon.

4.3.1.4. Establish Water Flow

Below are the steps for setting up water flow and important considerations to follow in order to avoid premature water running:

- Make sure that the water filter casing is securely in place and tightly closed.
- Connect the power cable from the sampler to the water distributor, but do not turn on the power yet.
- Connect the water supply hose to the water inlet port of the sampler.
- Close the water distributor's port to the sampler and open the other ports. Then, start the water flow.
- Use a temperature probe to check the temperature of the water. If the water temperature is above 60°C, it is safe to let the water flow into the sampler.
- Open the valve at the distributor (to the sampler) slowly, while monitoring "Pulse Channel 2 (Water Flow)," "Temperature," and "Pressure 1 (Water Pressure)."
- Do not let 100% of the water flow directly to the sampler from the beginning as too much water pressure may damage the contactor. Use the distributor outlets to reduce/control the flow to the sampler.
- A water flow rate of 10-15 L/min is suitable for sampling.

As was noted in the previous section, the presence of bubbles can be problematic and may have a significant impact on the final isotopic analysis results in certain cases. Therefore, it is important to verify the absence of bubbles after establishing the water flow in the field, using the methods and criteria listed below for confirmation.

- If there are bubbles at water tube connection, outside air might be being sucked in by the water flow. To prevent the sample from being contaminated by air bubbles, the opening should be located and closed promptly.

- If bubbles are still visible in the water filter or the water tubes after removing any possible leaks, it is possible that these bubbles are the result of gas exsolution from the water during decompression of gas-rich water. In such cases, these bubbles should be considered as part of the sample that needs to be collected. At this stage, there is no effective way to control or prevent the formation of such bubbles, and it is generally not necessary to do so.
- It is important to ensure that the sampling equipment and procedures are designed to minimize any potential contamination of the sample by external sources. If uncertainty exists regarding the origin of bubbles, increasing the back pressure of the water by slightly closing the water outflow control valve may help to clarify whether the bubbles are due to water-related factors or leaks. If the number of bubbles decreases under these conditions, it suggests that the bubbles are derived from the water and not associated with any leaks in the sampling system.

4.3.2. Gas Flow Connection

Valves at front panel are to control gas flows. Two positions (90 degrees apart) to open and close the flow. After the last sampling, all valves should have been closed, as previously shown in Fig. 27.

4.3.2.1. Connect Sampling Bag to the sampler

- Fill the water bucket with water from the sampling well.
- Tie a string from the weight to the stem of the valve, making sure to route the string below the valve connector.
- Apply a thin layer of vacuum grease to the stem.
- Connect a plastic tube from V4 to the stem, being careful not to turn the knob on the sampling bag.
- Submerge the sampling bag's valve and the plastic tube connection into the water bucket to prevent contamination from the atmosphere during sampling.
- Adjust the length of the string from the weight to keep the valve always underwater during sampling.

4.3.2.2. Establish the gas flow path and initial pumping

- Make sure the water trap is free of any remaining water. If there is water present, remove it by detaching the trap. To detach the trap, slide down the black knob and give it a 45-degree counter-clockwise turn. Check that the rubber gasket is not damaged. To reattach the trap, follow the same steps in reverse, making sure the black knob is securely locked in place with a clicking sound.
- Make sure that the vent valve is closed (Fig. 33).

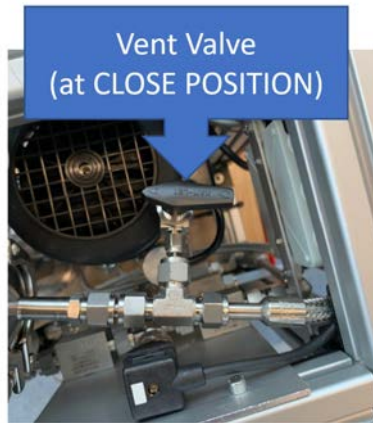


FIG. 33. Vent valve at its close position located on the top of the device.

4.3.2.3. Initial Pump Down and Leak Test

- Configure the valve conditions according to Fig. 34. Ensure that the small valve located at the sample bag remains closed. Observe the pressures P2 and P3 as they drop; both should register below <20 mbar when the system is dry. Commence the vacuum pump by pressing the designated button and monitor the pressures P2 and P3, which should continue to decline.

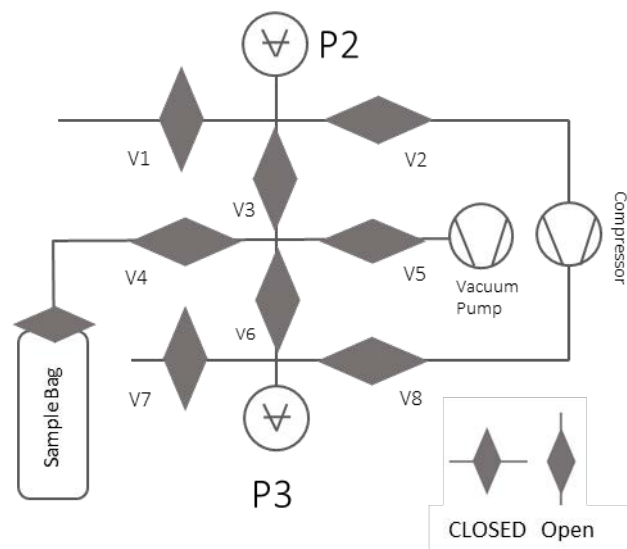


FIG. 34. Status of the valves before the initial pump down.

- Once this is done, close V4 and V5, and keep an eye on P2 and P3. If P2 stays below 20 mbar for a duration of 10 minutes, then the system is deemed leak-tight and in good working order. Record the values of P2 and P3 in the sampling log sheet.
- Next, reopen V4 and V5 and observe as the pressure drops to the baseline. Proceed to close V5 for a leak test on the transparent tube that connects to the sampling bag. It is important to ensure that the connection is not excessively leaky during this testing stage, as a vacuum in the tube can cause pressure increases in P2/P3, which is normal.
- If P2 stays below 30 mbar for a period of 5 minutes, then the system is deemed suitable for sampling. It is important to note that during sampling, pressure is maintained at

atmospheric levels, and the connection will be submerged in water, eliminating the possibility of air leakage into the bag.

- After completing the previous steps, proceed to set the valves according to the configuration shown below (Fig. 35). This involves closing V3 and V6, and opening V7 and V5.

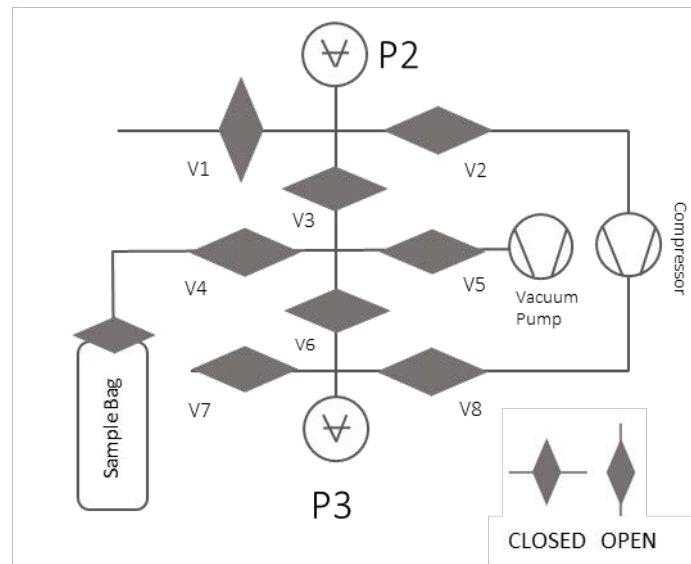


FIG. 35. Status of the valves before flushing the sampler's internal volume with the sample gas.

- Next, start the compressor and monitor the pressure readings. P2 should indicate a vacuum pressure of 50-60 hPa or lower if the system is dry, while P3 should remain at atmospheric pressure (~1000 hPa).
- Fill a container with the sampling water.
- Securely attach the transparent tube to the gas exhaust port (located at V7) using a hose clamp.
- Check that P3 is reading atmospheric pressure. Next, submerge the opposite end of the transparent tube into the container of water.

4.3.3. Flushing

To minimize the potential contamination of the sample with residual air in the system, it is necessary to flush the gas manifolds and compressor with gas extracted from the sample water. Follow these steps:

- Ensure that there is no water leakage, particularly at the connections.
- Verify that P2 is reasonably low, below 20 hPa, and that P3 is at atmospheric pressure.
- The water vapor trap should be correctly attached.
- Slowly begin to open V1, being mindful of the intense bubbling at the water reservoir at the gas exhaust - this is normal.
- When opening V1, give the smallest possible move and keep P2 below 200 hPa.
- When V1 is fully open, leave it for 5 minutes to fill the system with the sample gas. You should see bubbles in the water reservoir that are from the sample.

4.3.4. Purging

In this step, we will purge the gas sampling tube with sample gas by switching from exhaust flow to flow into the sample container. Follow the steps below:

- Ensure that the valve configuration is as shown in Fig 36 before proceeding with this step.

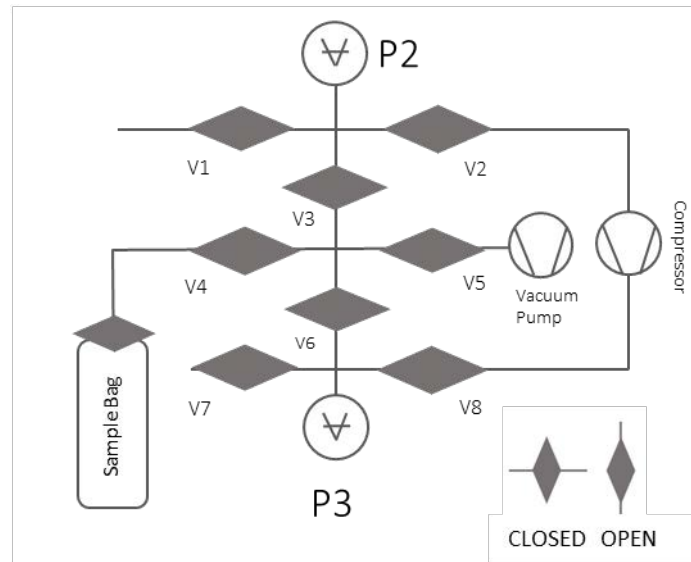


FIG. 36. Status of the valves before the purging.

- Close V5 to isolate the pump.
- Fold the transparent tube at V7 with one hand while keeping the other end inside the water to prevent water from flowing back into the compressor during the next step.
- Slowly open V6 and wait for P3 to be greater than atmospheric pressure. At this stage, the valve configuration is as shown below (Fig. 37).

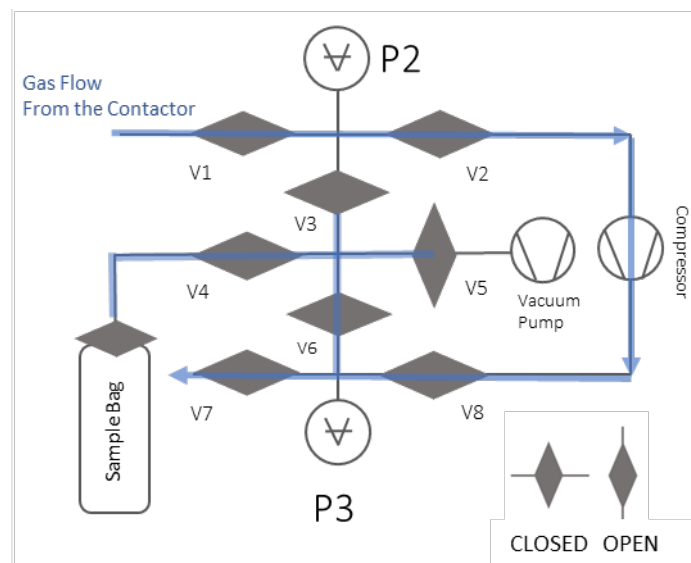


FIG. 37. Status of the valves during the purging (blue area is purged with sample).

- Then, unfold the transparent tube slowly and let it bubble in the water again.
- Wait for 2 minutes to complete the purging process.

4.3.5. Sample Gas Collection

4.3.5.1. Sample Gas Collection (1st bag)

To collect a water sample, follow these steps:

- Open the screw cap valve of the sampling bag while it is underwater to prevent air from entering.
- Close valve V7 (make sure the valves are in their positions as shown in Fig. 38)

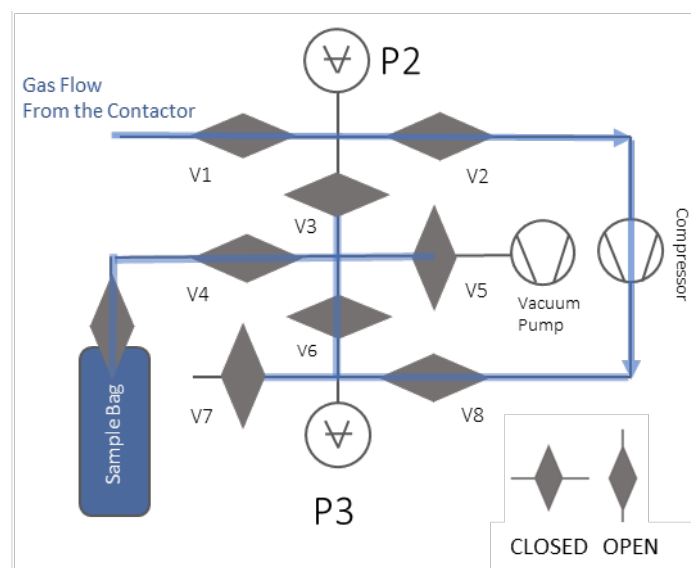


FIG. 38. Status of the valves during the sampling

- Monitor pressure gauge P2 and ensure the water levels in the vapor traps are being watched. Pressure gauge P3 should always indicate atmospheric pressure. Do not pressurize the bag - fill it up to around 80% capacity to prevent rupture during air transport.
- Take a picture of the sampling bag after collecting the water sample.

The following precautions should be taken when collecting a water sample:

- P2 may slowly increase during the sampling process, which can cause P3 to rise more slowly as well. Unfortunately, there is no way to fix this during the sampling.
- In some cases, P2 may drop again, but sometimes it may remain high. If the pressure reaches 500 hPa, you can try closing valve V1 and observing P2 to see if it drops. If it does, you can then slowly open valve V1 to keep P2 low. However, if P3 is not rising, it is important to remain patient and wait until you reach the targeted pressure.
- When the sample bag is about 80% full, hand-tighten the screw cap valve and remove the bag from the water bucket.
- Open valve V7 to allow bubbling, and then close valve V6.

- To indicate that the cylinder has a sample inside, place a piece of sticky tape over the valve on the sampling bag. Then, write down the sample ID, date, and time.
- This marks the end of the first sampling bag.

4.3.5.2. Sample Gas Collection (2nd bag)

Follow below steps to proceed to gas collection into the 2nd sampling bag:

- Apply vacuum grease on the sampling tube from V4 and connect the 2nd sampling bag. Open V5 to initiate the evacuation process. Close V1 and V2, and Open V3 to read P2.
- If P2 is less than 20 mbar, perform a quick leak check by closing V5 and monitoring P2 using the same criteria as in the leak check section.
- After checking the pressure and leak, close V3, open V2, and slowly open V1 to observe the bubbling.
- Attach the string and weight to the valve connection and submerge it into the water. The valve configuration at this stage is shown in Fig. 39.

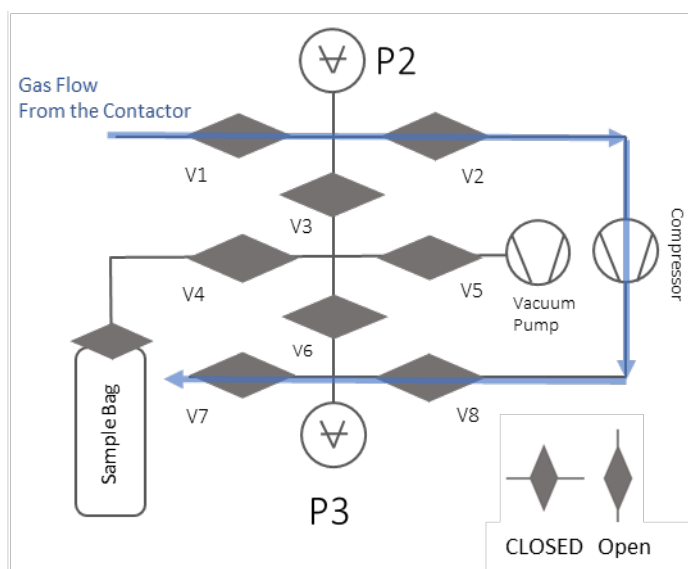


FIG. 39. Status of the valves before the purging before sampling into the second bag.

To purge the system, follow these steps:

- Close V5 to isolate the pump.
- With one hand, fold the transparent tube at V7 while the other end is still submerged in the water to prevent water from flowing back into the compressor during the next step.
- Slowly open V6 and wait for P3 to be greater than atmospheric pressure.
- Unfold the transparent tube slowly and let it bubble in the water again. At this stage, the valves should be in the positions shown in Fig. 37.
- Wait for 2 minutes for purging to complete before starting the sampling.
- Open the screw cap valve of the sampling bag while it's submerged in water.
- Close V7 and monitor P2 while also keeping an eye on the water levels in the vapor traps.
- Make sure that P3 remains at atmospheric pressure.
- Avoid over-inflating the bag to prevent rupturing during air transport. Fill it up to about 80% of its capacity and wait until the bag is filled, but do not fully inflate it.

4.3.5.3. *Post-Sampling Procedures*

- Close the screw cap valve on the sampling bag (hand-tight) and remove the bag from the water bucket.
- Remove the transparent tube from the water reservoir and open V7.
- Remove the transparent tube from the exhaust port at V7.
- Seal the sampling bag's valve with sticky tape and label the bag with the sample ID, date, and time.
- Stop the water flow from the well to the sampler.
- Close V6.
- Ensure that the sampling tube is not underwater, then open V5 to allow air to pass through the vacuum pump.
- Open the vent valve and empty the water reservoir of the trap if there is any water inside.
- Provide some back pressure to enhance water removal from the compressor by repeatedly opening and closing V7 or using your thumb to close the exhaust or run the compressor for a while.
- Turn off the compressor, pump, and main switch, and disconnect the power cable.
- Disconnect the water inlet tube from the sampler and cover the electrical parts of the sampler.
- Disconnect the water outlet tube from the sampler and cover the electrical parts of the sampler.
- Remove the water filter casing, empty it, and rinse the filter cartridge if it is dirty. Replace the filter cartridge with a new one for the next sampling.
- Drain water from the contactor by opening the bottom flange at the contactor cartridge to remove water from it. Ensure not to lose the rubber gasket.

This is the end of the procedure.

5. KRYPTON PURIFICATION FOR ATTA

After collecting dissolved gas samples in the field as described in Section 4, the subsequent step for ATTA krypton analysis involves creating a pure krypton sample of several μL from roughly 10 L of bulk gas samples collected in the field. Laboratories utilize purpose-built devices for purification of krypton, with configurations differing among different facilities. This section provides an overview on the krypton purification system developed at the IHL (Fig. 40) which has been used to making purified krypton samples for ATTA analysis for several projects carried out in the CRP.

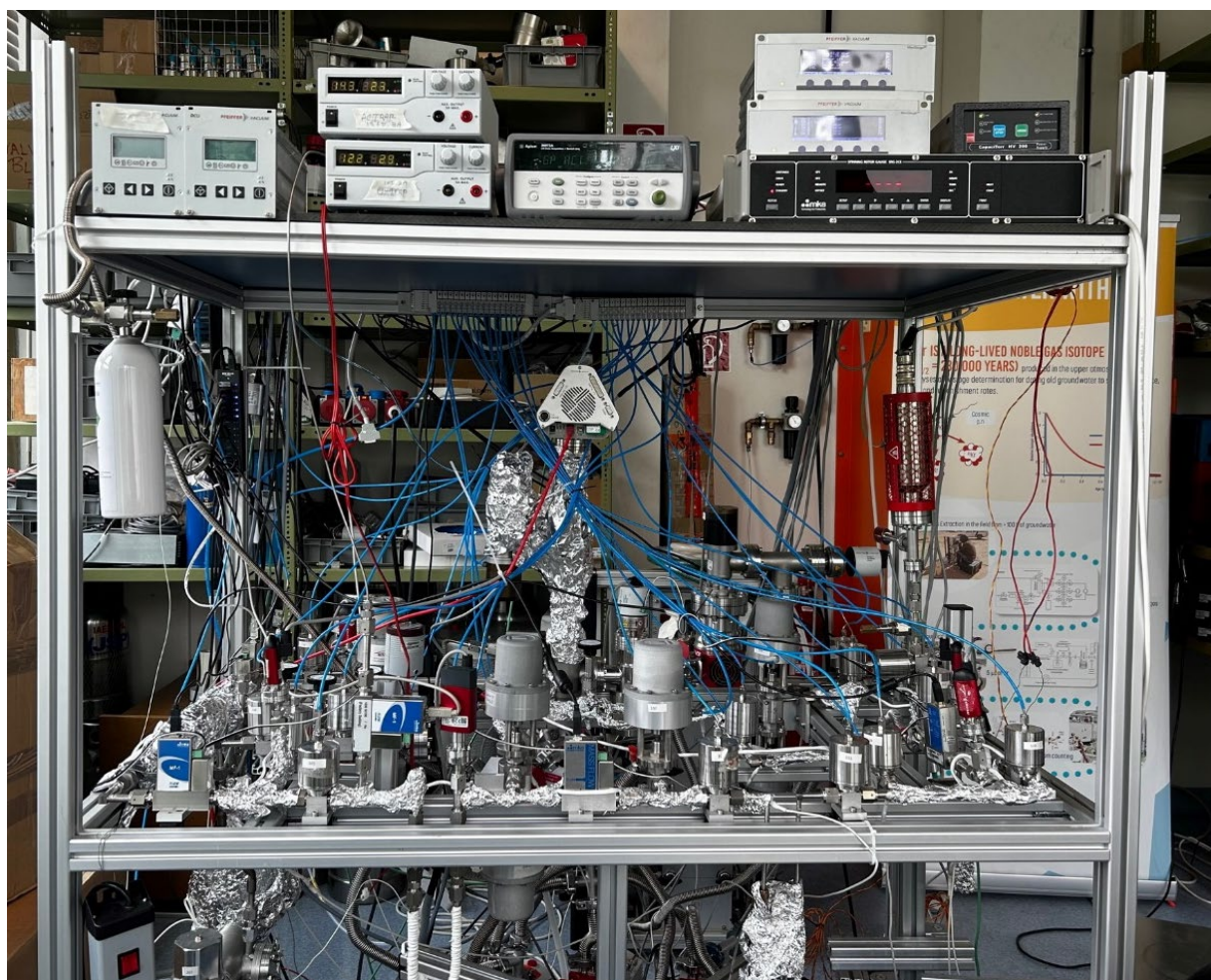


FIG. 40. Krypton purification system designed and built at the IHL, IAEA.

5.1. SYSTEM CONFIGURATION

Figure 41 presents a schematic diagram detailing the krypton purification system utilized at the IHL, IAEA. This specialized system is designed to extract and purify krypton from gas samples collected in groundwater fieldwork, and the entire purification process typically spans a duration of approximately 3 to 4 hours. The system features a high-vacuum, all-metal line and incorporates key components, including pneumatic valves, mass flow controllers, a $\text{CO}_2\text{-H}_2\text{O}$ vapor absorber, activated charcoal (AC) traps, a GC column, and a high-capacity getter pump. During operation, the quadrupole mass spectrometer is used to dynamically monitor gas composition and estimate the purity and amount of krypton in the final product. To enhance operational efficiency and reduce the need for constant human intervention, the system is

controlled by a LabView program, which both logs and manages the purification procedure. The purification process itself can be divided into three distinct stages, namely, cryogenic distillation, GC, and the final purification step aimed at producing a sample of pure krypton.

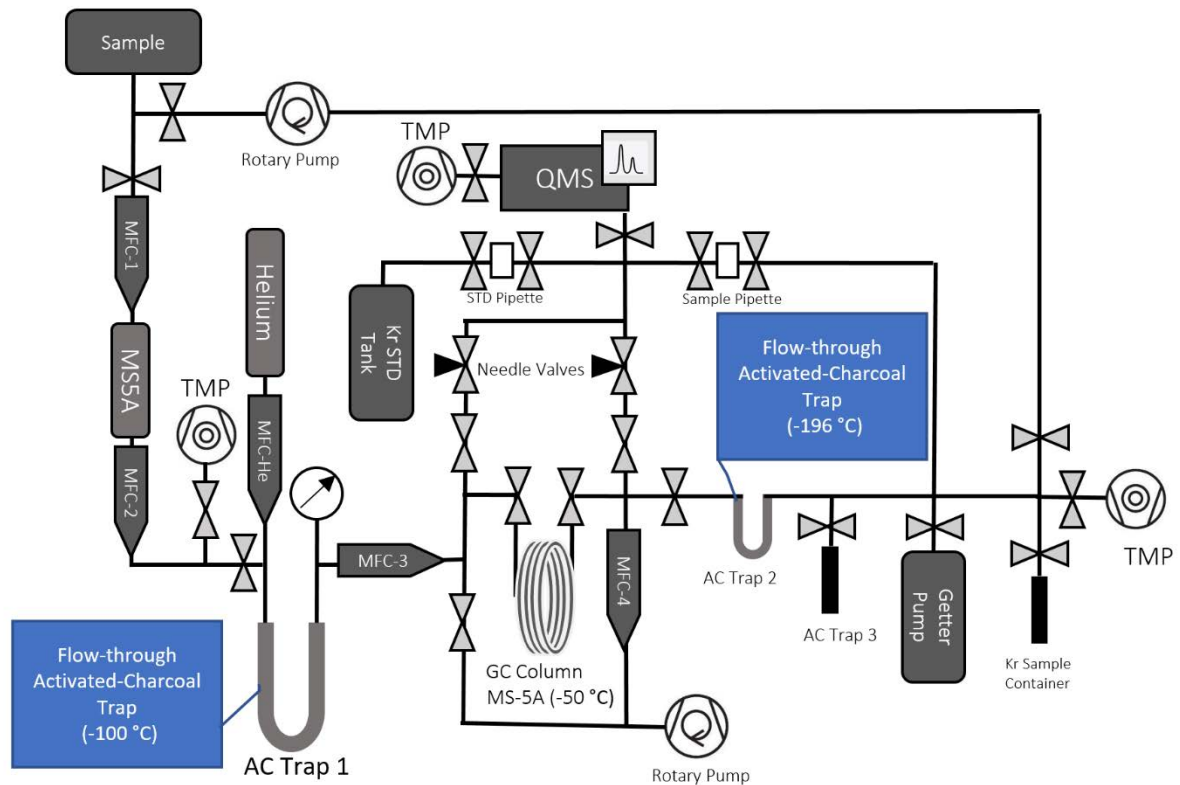


FIG. 41. A schematic representation of the IAEA's krypton purification system, with the following abbreviations: Mass Flow Controller (MFC), Turbo Molecular Pump (TMP), Activated Charcoal (AC), Gas chromatography (GC), and Standard Gas (STD). Modified from [28].

5.2. CRYOGENIC DISTILLATION

The process for initial rough separation involves cryogenic distillation. The procedure starts by introducing the sample gas into the system at a flow rate of $200 \text{ cm}^3/\text{min}$, regulated by the Mass Flow Controller (MFC1) at the sample inlet port, as shown in Fig. 41. The gas first passes through a $\text{CO}_2\text{-H}_2\text{O}$ vapor absorber and then enters AC Trap 1. The operating temperature of AC Trap 1, either $-196 \text{ }^\circ\text{C}$ with liquid nitrogen or $-100 \text{ }^\circ\text{C}$ using a methanol-liquid nitrogen mix, depends on the total gas sample volume. This trap, a U-shaped stainless-steel tube with a 10 mm inner diameter and containing 6.6 grams of activated charcoal, is temperature-controlled by an external heating wire and a temperature sensor. The gas leaving AC Trap 1 is evacuated through the Mass Flow Controller 3 (MFC 3) with the flow regulated at $200 \text{ cm}^3/\text{min}$. This step primarily removes nitrogen and some argon, while krypton is adsorbed in AC Trap 1. After loading the predetermined amount of sample gas, MFC1 and MFC2 are closed to stop further gas entry. Distillation continues with MFC3 open to the rotary pump, reducing the pressure in the trap's headspace below 1 mbar. AC Trap 1 is kept at $-100 \text{ }^\circ\text{C}$ during this vacuum distillation, which typically lasts 60 minutes.

Finally, to release krypton completely, AC Trap 1 is disconnected from the pump and heated to 120 °C for about 10 minutes until the pressure stabilizes. With an initial 5 liters of sample gas, the remaining gas volume is reduced to approximately 20 cm³. This residual gas is then subjected to further purification using gas chromatography (GC).

After loading the specified amount of sample gas, we close MFC1 and MFC2 to block further entry of the sample gas. The distillation process then proceeds by keeping MFC3 open to the rotary pump. This action continues until the pressure in the headspace of the trap falls below 1 mbar. Throughout this phase, we maintain AC Trap 1 at a temperature of -100 °C, and this vacuum distillation phase typically spans about 60 minutes.

Following this, to ensure that all krypton is released from AC Trap 1, we isolate the trap from the pump and heat it to 120 °C. This heating is maintained for roughly 10 minutes or until the pressure reading stabilizes. After processing a total of 5 liters of sample gas, the remaining gas in the system is condensed to about 20 cm³. This reduced volume of gas is then subjected to further purification using gas chromatography (GC).

5.3. GAS CHROMATOGRAPHY

The GC column, a stainless-steel coil packed with 60-80 mesh MS-5A, is used to separate krypton from other gases. This column is cooled in a methanol bath using an immersion chiller to keep it at the desired temperature. Helium, serving as the carrier gas, flows through the system at a rate of 50 cm³/min. To observe the effluents emerging from the GC, we use a Quadrupole Mass Spectrometer (QMS), which operates in a dynamic vacuum. This vacuum condition is maintained by a needle valve to continuously inlet small fraction of the gas effluents to the QMS. With the GC temperature kept at -60 °C, the concentration of non-krypton species in the effluents diminishes, almost reaching baseline levels (Fig. 42). Subsequently, the gas flow path is reconfigured to channel the krypton into a liquid-nitrogen-cooled activated charcoal trap (AC Trap 2). At the operating temperature of the GC column, it is important to note that the residual nitrogen (N₂) from AC Trap 1 migrates very slowly, requiring several hours for its complete evacuation from the column.

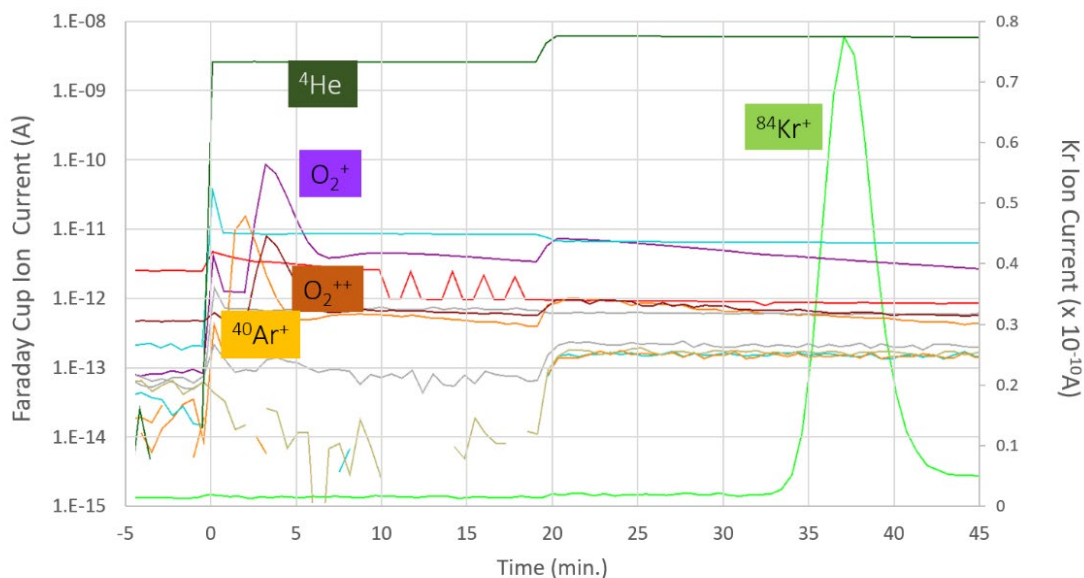


FIG. 42. Illustration of gas chromatography results for an air sample following the vacuum distillation process, analyzed using the QMS. At the 20-minute mark, the effluent flow path was transitioned from evacuation to collection. The observed shifts in QMS signals at this juncture are attributed to the alteration in total pressure within the processing line, caused by the change in gas conductance as it shifts from MFC-4 to the collection trap.

After the GC process, the fraction retained at the AC Trap 2 consist mainly with krypton with some residual argon. If the argon peak is equal to or greater than that of krypton, a second separation and distillation process is initiated using AC Trap 3, which is maintained at a cooling temperature of -100°C . At this temperature, more than 99% of the krypton is captured by the activated charcoal, while helium and a significant portion of the argon remain in the headspace. This secondary distillation process significantly enhances the purity of krypton in the final processed sample. In the case of groundwater samples, the purity of krypton exceeds 90%, as indicated by the QMS spectrum (see Fig. 43). Finally, the krypton-rich fraction is transferred into the final krypton container, which contains 40 mg of activated charcoal and is cooled to -196°C .

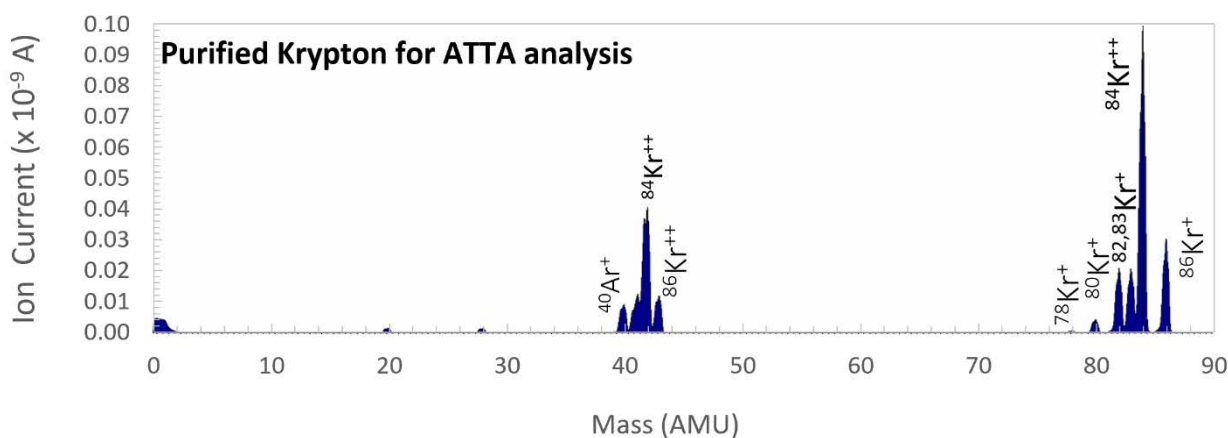


FIG. 43. Mass spectra of the final product of the krypton purification system at the IAEA. In an entire mass range, peaks of krypton isotopes are predominant.

As detailed in Romeo et al., [28], the absolute amount of purified krypton is determined by analyzing a pipetted aliquot (0.4 cm^3) of purified krypton using the sample pipette, which is introduced to the QMS under static vacuum. To calibrate the sensitivity of the QMS, a pipetted aliquot of krypton standard gas is measured before and after the sample analysis. Recovery yields of krypton determined by processing air samples were 70 to 95 % [28]. The higher recovery yield was achieved by using the lower temperatures ($-196 \text{ }^\circ\text{C}$) for the initial trapping at the AC trap 1 than $-100 \text{ }^\circ\text{C}$ as described above. However, the lower trapping temperature required a longer time for the initial vacuum distillation. Thus, the choice of trapping temperature depends on the available sample size and time constraints. Further details about the system are presented in [28].

5.4. METHANE REMOVAL METHOD

In certain instances, methane gas can comprise a significant portion of dissolved gases in groundwater. This can occur naturally or because of human activities such as coal mining, gas well drilling, pipeline leaks, and landfill operations. The presence of methane poses a challenge in the purification of krypton, as the commonly used GC column fails to effectively separate krypton from methane. Consequently, one potential approach to purify krypton from a methane-rich gas sample involves removing methane from the sample prior to the processing.

Figure 44 illustrates the configuration of the methane removal system developed at the Central Research Institute of Electric Power Industry (CRIEPI). This system employs an "oxidation method" wherein methane present in the gas sample is oxidized to generate H_2O and CO_2 . The system has the capacity to oxidize approximately 50 L of gas and utilizes suitable absorbents to eliminate H_2O and CO_2 . It consists of a copper oxide column for methane combustion, a molecular sieve column for water removal, and a gas bag with a CO_2 absorbent to concentrate krypton. To ensure thorough oxidation, two tube reactors containing copper oxide are connected in series. The carbon dioxide absorbent is housed in an aluminium bag, into which all other constituents, including krypton, are advectively transported by a CO_2 flow towards the gas bag.

By allowing the methane-rich gas (90% in volume) to pass through the system, the total gas volume in the final sampling bag can be reduced to approximately 1/100th of the original volume. The resulting product contains only 0.1% methane. Consequently, the krypton concentration becomes roughly 100 times higher than that in the unprocessed gases [48].

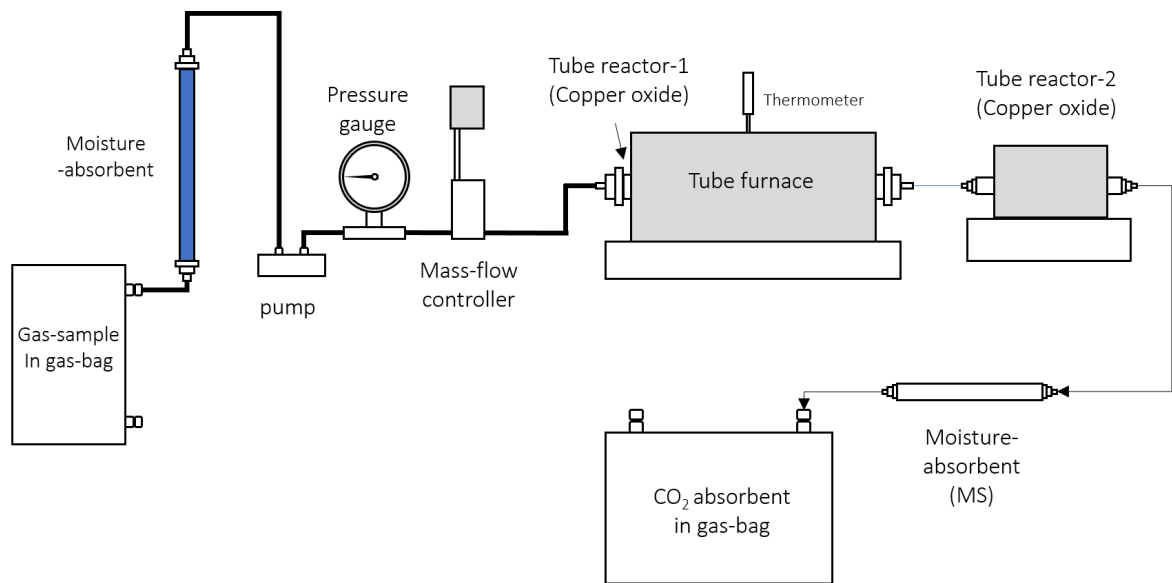


FIG. 44. CH₄ removal system at the Central Research Institute of Electric Power Industry (CRIEPI)

6. DATA REDUCTION IN ^{81}Kr ANALYSIS OF GROUNDWATER SAMPLES

This section outlines the protocol for calculating ^{81}Kr ages based on the analytical results obtained through ATTA. It also discusses the methods used to correct for the impact of atmospheric contamination and estimate errors

6.1. AGE CALCULATION

The ^{81}Kr abundance relative to the modern atmospheric value is denoted R_{81} . This is the ratio between the $^{81}\text{Kr}/\text{Kr}$ of the sample and the $^{81}\text{Kr}/\text{Kr}$ of the air. For a present-day sample, $R_{81} = 1$. The ^{81}Kr -age of the sample can be calculated as follows,

$$^{81}\text{Kr age} = -t_{1/2} \cdot \ln(R_{81}) / \ln 2 \quad (1)$$

where $t_{1/2} = 229 \pm 11$ ka is the half-life of ^{81}Kr .

When the measured R_{81} value falls well between 0 and 1, the apparent age with an error σ (one standard deviation) is calculated according to equation (1). When R_{81} is close to 1, an upper age limit is calculated. The age of the sample has a 90% probability of being younger than (i.e. less than) the upper limit. Similarly, when R_{81} is low and close to the detection limit (~ 0.02), a lower age limit is calculated. The sample has a 90% probability to be older than (more than) the lower age limit.

6.2. AGE CORRECTION

For cases of $R_{81} < 1$, the sample is too old for any original ^{85}Kr to be present, thus the ^{85}Kr decay activity (denoted R_{85}) is expected to be zero. Any presence of ^{85}Kr indicates a mixture of young or modern gas sources, and a correction should be made in the age calculation. The contamination can come from different sources: 1) Mixing with young groundwater (age < 50 a). Additional information about the source of mixture is needed to obtain the ages of different end members. 2) Mixing with air during the gas extraction and purification process. Air can be introduced into the groundwater and contaminate the gas sample in the well head or in the pumping system. In addition, leaks can occur in the degassing system or the sample bottle.

For case 2), effects of air contamination can be corrected. The relationship between the corrected ^{81}Kr abundance (R_{81_corr}) and the measured ^{81}Kr abundance (R_{81_meas}), both relative to the modern air value, is

$$R_{81_meas} = R_{81_corr} \times (1-\eta) + \eta \quad (2)$$

where η is the fraction of the krypton coming from modern contaminants. The contamination fraction η can be extracted using the measured ^{85}Kr activity (R_{85_meas}) and the ^{85}Kr activity of the local air at the sampling site (R_{85_air}):

$$R_{85_meas} = R_{85_air} \times \eta \quad (3)$$

By combining Eq. (2) and (3), the corrected ^{81}Kr abundance (R_{81_corr}) can be calculated.

6.3. ATMOSPHERIC HISTORY OF ^{81}Kr

^{81}Kr is a cosmogenic isotope. Its production rate is directly related to the flux of the incoming cosmic ray particles. Since the cosmic ray intensity on earth varies with time, the ^{81}Kr abundance in the atmosphere is not a constant. Based on the relative geomagnetic field intensities recorded over the past 2 Ma [49], the atmospheric $^{81}\text{Kr}/\text{Kr}$ abundance has been calculated in [50]. Based on this ^{81}Kr input history, corrections can be made to the ^{81}Kr ages calculated directly from the decay equation (Eq. 1). Figure 45 shows the input correction versus the ^{81}Kr age calculated directly with Eq. 1. The relative uncertainty of this correction is estimated to be smaller than 5%.

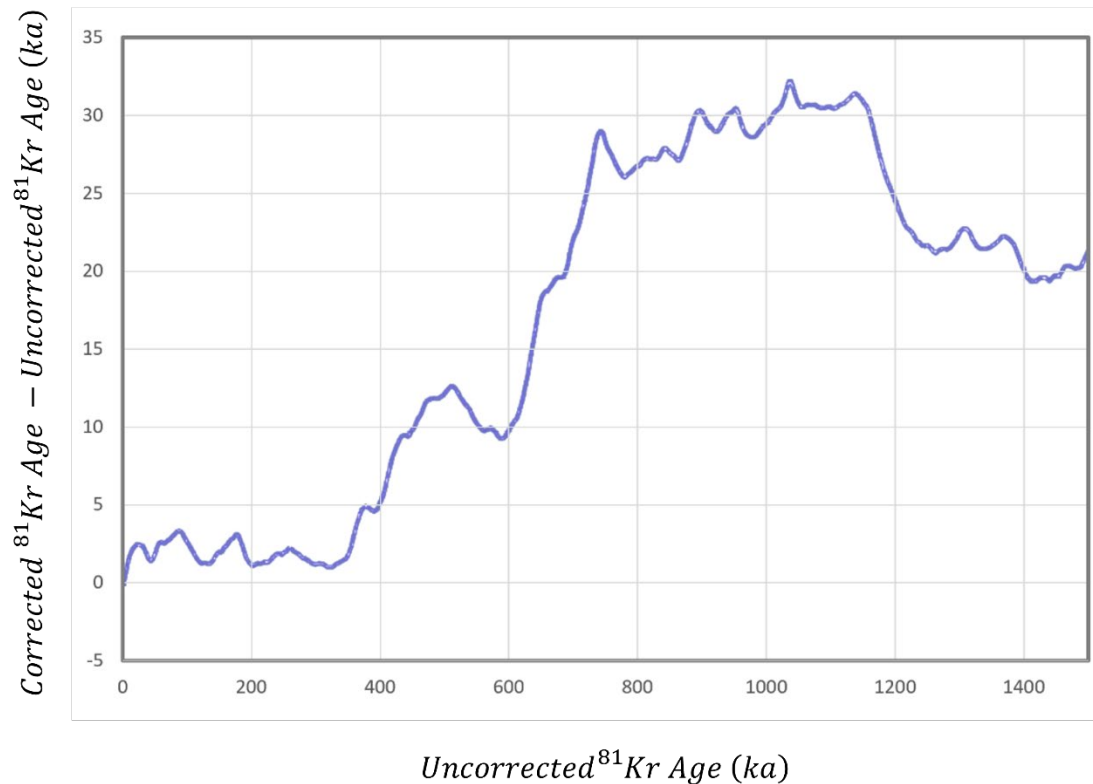


FIG. 45. ^{81}Kr age correction based on the atmospheric input history of ^{81}Kr .

6.4. ERROR ESTIMATION

Several sources contribute to the uncertainty estimation:

- Statistical errors of atom counting of ^{81}Kr and ^{85}Kr . When the results are near the physical boundaries, we adopt the Feldman-Cousins method for error estimation [51].
- Systematic error due to the uncertainty of the half-life 229 ± 11 ka. This error causes the calculated ^{81}Kr ages to shift together for all samples. It affects older sample more significantly.
- The correction procedure described above contributes additional uncertainties.

UTSC ATTA results are reported with error of a 1σ standard deviation. When reporting upper or lower limits, the confidence level is set to be 90%.

6.5. SUMMARY

In this section, data reduction methods for analyzing groundwater samples using ^{81}Kr were presented. Age calculation was performed based on the relative abundance of ^{81}Kr compared to the modern atmospheric value, referred to as R_{81} . It was also noted that the utility of analyzing ^{85}Kr activity in identifying potential contamination from contemporary air and making appropriate corrections to R_{81} . Furthermore, corrections were made considering the atmospheric history of ^{81}Kr . Error estimation encompassed statistical errors, systematic errors associated with the half-life of ^{81}Kr , and additional uncertainties stemming from the correction procedure. The reported results included a 1σ standard deviation, with upper or lower limits presented at a 90% confidence level. For more information on ATTA analysis, please refer to the "ATTA Primer" webpage¹ as a reference.

¹ <http://atta.ustc.edu.cn/en-us/events/attaprimer.html>

REFERENCES

- [1] KROEZE, C., GABBERT, S., HOFSTRA, N., KOELMANS, A.A., LI, A., LÖHR, A., LUDWIG, F., STROKAL, M., VERBURG, C., VERMEULEN, L., VAN VLIET, M.T.H., DE VRIES, W., WANG, M., VAN WIJNEN, J., Global modelling of surface water quality: a multi-pollutant approach. *Current Opinion in Environmental Sustainability*. **23** (2016) 35-45.
- [2] RODELL, M., FAMIGLIETTI, J.S., WIESE, D.N., REAGER, J.T., BEAUDOING, H.K., LANDERER, F.W., LO, M.H., Emerging trends in global freshwater availability. *Nature*. **557** (2018) 651-659.
- [3] FAMIGLIETTI, J.S., The global groundwater crisis. *Nature Climate Change*. **4** (2014) 945-948.
- [4] FOSTER, S., Global Policy Overview of Groundwater in Urban Development—A Tale of 10 Cities! *Water*. **12** (2020) 456.
- [5] WADA, Y., VAN BEEK, L.P.H., VAN KEMPEN, C.M., RECKMAN, J.W.T.M., VASAK, S., BIERKENS, M.F.P., Global depletion of groundwater resources. *Geophysical Research Letters*. **37** (2010).
- [6] HAN, D., KOHFAHL, C., SONG, X., XIAO, G., YANG, J., Geochemical and isotopic evidence for palaeo-seawater intrusion into the south coast aquifer of Laizhou Bay, China. *Applied Geochemistry*. **26** (2011) 863-883.
- [7] JIA, X., O'CONNOR, D., HOU, D., JIN, Y., LI, G., ZHENG, C., OK, Y.S., TSANG, D.C.W., LUO, J., Groundwater depletion and contamination: Spatial distribution of groundwater resources sustainability in China. *Science of The Total Environment*. **672** (2019) 551-562.
- [8] KONIKOW, L.F., KENDY, E., Groundwater depletion: A global problem. *Hydrogeology Journal*. **13** (2005) 317-320.
- [9] YE, S., XUE, Y., WU, J., YAN, X., YU, J., Progression and mitigation of land subsidence in China. *Hydrogeology Journal*. **24** (2016) 685-693.
- [10] BETHKE, C.M., JOHNSON, T.M., Groundwater Age and Groundwater Age Dating. *Annual Review of Earth and Planetary Sciences*. **36** (2008) 121-152.
- [11] KPEGLI, K.A.R., ALASSANE, A., VAN DER ZEE, S.E.A.T.M., BOUKARI, M., MAMA, D., Development of a conceptual groundwater flow model using a combined hydrogeological, hydrochemical and isotopic approach: A case study from southern Benin. *Journal of Hydrology: Regional Studies*. **18** (2018) 50-67.
- [12] DE VRIES, J.J., SIMMERS, I., Groundwater recharge: an overview of processes and challenges. *Hydrogeology Journal*. **10** (2002) 5-17.
- [13] KWOYIGA, L., STEFAN, C., Institutional Feasibility of Managed Aquifer Recharge in Northeast Ghana. *Sustainability*. **11** (2019) 379.
- [14] HADJ AMMAR, F., DESCHAMPS, P., CHKIR, N., ZOUARI, K., AGOUNE, A., HAMELIN, B., Uranium isotopes as tracers of groundwater evolution in the Complexe Terminal aquifer of southern Tunisia. *Quaternary International*. **547** (2020) 33-49.
- [15] KÖLBEL, L., KÖLBEL, T., MAIER, U., SAUTER, M., SCHÄFER, T., WIEGAND, B., Water–rock interactions in the Bruchsal geothermal system by U–Th series radionuclides. *Geothermal Energy*. **8** (2020) 24.

- [16] MATSUMOTO, T., CHEN, Z., WEI, W., YANG, G.-M., HU, S.-M., ZHANG, X., Application of combined ^{81}Kr and ^4He chronometers to the dating of old groundwater in a tectonically active region of the North China Plain. *Earth and Planetary Science Letters*. **493** (2018) 208-217.
- [17] JIANG, W., BAILEY, K., LU, Z.T., MUELLER, P., O'CONNOR, T.P., CHENG, C.F., HU, S.M., PURTSCHERT, R., STURCHIO, N.C., SUN, Y.R., WILLIAMS, W.D., YANG, G.M., An atom counter for measuring ^{81}Kr and ^{85}Kr in environmental samples. *Geochimica et Cosmochimica Acta*. **91** (2012) 1-6.
- [18] LU, Z.T., SCHLOSSER, P., SMETHIE, W.M., STURCHIO, N.C., FISCHER, T.P., KENNEDY, B.M., PURTSCHERT, R., SEVERINGHAUS, J.P., SOLOMON, D.K., TANHUA, T., YOKOCHI, R., Tracer applications of noble gas radionuclides in the geosciences. *Earth-Science Reviews*. **138** (2014) 196-214.
- [19] LU, Z.-T., MUELLER, P., Chapter 4 - Atom Trap Trace Analysis of Rare Noble Gas Isotopes, in *Advances In Atomic, Molecular, Optical Physics*, P. Berman, E. Arimondo, C. Lin, Editors. (2010), Academic Press. p. 173-205.
- [20] MATSUMOTO, T., SILOMON, K.D., ARAGUÁS-ARAGUÁS, L., AGGARWAL, P., The IAEA's Coordinated Research Project on "Estimation of Groundwater Recharge and Discharge by Using the Tritium, Helium-3 Dating Technique": In Lieu of a Preface. *Geochemical Journal*. **51** (2017) 385-390.
- [21] HAN, L.-F., ROLLER-LUTZ, Z., HUNJAK, T., LUTZ, H.O., MATSUMOTO, T., AGGARWAL, P., Groundwater responses to recharge in the Gacka Area, Croatia, as revealed by stable isotopes, tritium, CFCs and noble gases. *Geochemical Journal*. **51** (2017) 391-407.
- [22] DARLING, W.G., GOODDY, D.C., WHITE, D., MATSUMOTO, T., HAN, L.-F., ROMEO, N., Testing tritium-helium groundwater dating in the Chalk aquifer of the Berkshire Downs, UK. *Geochemical Journal*. **51** (2017) 423-437.
- [23] JANKOVEC, J., VITVAR, T., ŠANDA, M., MATSUMOTO, T., HAN, L.-F., Groundwater recharge and residence times evaluated by isotopes of hydrogen and oxygen, noble gases and CFCs in a mountain catchment in the Jizera Mts., northern Czech Republic. *Geochemical Journal*. **51** (2017) 423-437.
- [24] PALCSU, L., KOMPÁR, L., DEÁK, J., SZŰCS, P., PAPP, L., Estimation of the natural groundwater recharge using tritium-peak and tritium/helium-3 dating techniques in Hungary. *GEOCHEMICAL JOURNAL*. **51** (2017) 439-448.
- [25] KAMDEE, K., ALVARADO, J.A.C., OCCARACH, O., HUNYEK, V., WONGSIT, A., SAENGGORAKOT, C., CHANRUANG, P., C. POLEE, S.K., MATIATOS, I., MATSUMOTO, T., Application of isotope techniques to study groundwater resources in the unconsolidated aquifers along the Ping River (Thailand). *Isotopes in Environmental & Health Studies*. **56** (2020) 95-110.
- [26] AGGARWAL, P.K., MATSUMOTO, T., STURCHIO, N.C., CHANG, H.K., GASTMANS, D., ARAGUAS-ARAGUAS, L.J., JIANG, W., LU, Z.-T., MUELLER, P., YOKOCHI, R., Continental degassing of ^4He by surficial discharge of deep groundwater. *Nature Geoscience*. **8** (2015) 35-39.

- [27] ZOUARI, K., MATSUMOTO, T., TRABELSI, R., AGGARWAL, P. Using Environmental Isotopes and Krypton-81 to Characterize and Date Continental Intercalaire Paleogroundwater (Southern Tunisia). In: ZHANG, Z., KHÉLIFI, N., MEZGHANI, A., HEGGY, E. (eds) Patterns and Mechanisms of Climate, Paleoclimate and Paleoenvironmental Changes from Low-Latitude Regions. CAJG 2018. Advances in Science, Technology & Innovation (2019) 61-63.
- [28] ROMEO, N., MABRY, J., HILLEGONDS, D., KAINZ, G., JAKLITSCH, M., MATSUMOTO, T., Developments of a field gas extraction device and krypton purification system for groundwater radio-krypton dating at the IAEA. Applied Radiation and Isotopes. **189** (2022) 110450.
- [29] PROBST, P., YOKOCHI, R., STURCHIO, N.C., Method for Extraction of Dissolved Gases From Groundwater for Radiokrypton Analysis. (2006). H41B-0414.
- [30] YOKOCHI, R., Recent developments on field gas extraction and sample preparation methods for radiokrypton dating of groundwater. Journal of Hydrology. **540** (2016) 368-378.
- [31] YOKOCHI, R., HERATY, L.J., STURCHIO, N.C., Method for purification of krypton from environmental samples for analysis of radiokrypton isotopes. Analytical Chemistry. **80** (2008) 8688-8693.
- [32] TU, L.-Y., YANG, G.-M., CHENG, C.-F., LIU, G.-L., ZHANG, X.-Y., HU, S.-M., Analysis of Krypton-85 and Krypton-81 in a Few Liters of Air. Analytical Chemistry. **86** (2014) 4002-4007.
- [33] PURTSCHERT, R., YOKOCHI, R., JIANG, W., LU, Z.T., MUELLER, P., ZAPPALA, J., VAN HEERDEN, E., CASON, E., LAU, M., KIEFT, T.L., GERBER, C., BRENNWALD, M.S., ONSTOTT, T.C., Underground production of ⁸¹Kr detected in subsurface fluids. Geochimica et Cosmochimica Acta. **295** (2021) 65-79.
- [34] KIPFER, R., AESCHBACH-HERTIG, W., PEETERS, F., STUTE, M., Noble Gases in Lakes and Ground Waters. Reviews in Mineralogy and Geochemistry. **47** (2002) 615-700.
- [35] TORGERSEN, T., Controls on pore-fluid concentration of ⁴He and ²²²Rn and the calculation of ⁴He/²²²Rn ages. Journal of Geochemical Exploration. **13** (1980) 57-75.
- [36] TORGERSEN, T., CLARKE, W.B., Helium accumulation in groundwater, I: An evaluation of sources and the continental flux of crustal ⁴He in the Great Artesian Basin, Australia. Geochimica et Cosmochimica Acta. **49** (1985) 1211-1218.
- [37] BETHKE, C.M., ZHAO, X., TORGERSEN, T., Groundwater flow and the ⁴He distribution in the Great Artesian Basin of Australia. Journal of Geophysical Research: Solid Earth. **104** (1999) 12999-13011.

- [38] AGGARWAL, P.K., MATSUMOTO, T., STURCHIO, N.C., CHANG, H.K., GASTMANS, D., ARAGUAS-ARAGUAS, L.J., JIANG, W., LU, Z.-T., MUELLER, P., YOKOCHI, R., PURTSCHERT, R., TORGERSEN, T., Continental degassing of ^4He by surficial discharge of deep groundwater. *Nature Geoscience*. **8** (2015) 35-39.
- [39] MÉJEAN, P., PINTI, D.L., KAGOSHIMA, T., ROULLEAU, E., DEMARETS, L., POIRIER, A., TAKAHATA, N., SANO, Y., LAROCQUE, M., Mantle helium in Southern Quebec groundwater: A possible fossil record of the New England hotspot. *Earth and Planetary Science Letters*. **545** (2020) 116352.
- [40] MATSUMOTO, T., CHEN, Z., WEI, W., YANG, G.-M., HU, S.-M., ZHANG, X., Application of combined ^{81}Kr and ^4He chronometers to the dating of old groundwater in a tectonically active region of the North China Plain. *Earth and Planetary Science Letters*. **493** (2018) 208-217.
- [41] ANDREWS, J.N., The isotopic composition of radiogenic helium and its use to study groundwater movement in confined aquifers. *Chemical Geology*. **49** (1985) 339-351.
- [42] AESCHBACH-HERTIG, W., STUTE, M., CLARK, J.F., REUTER, R.F., SCHLOSSER, P., A paleotemperature record derived from dissolved noble gases in groundwater of the Aquia Aquifer (Maryland, USA). *Geochimica et Cosmochimica Acta*. **66** (2002) 797-817.
- [43] PLUMMER, L.N., EGGLESTON, J.R., ANDREASEN, D.C., RAFFENSPERGER, J.P., HUNT, A.G., CASILE, G.C., Old groundwater in parts of the upper Patapsco aquifer, Atlantic Coastal Plain, Maryland, USA: evidence from radiocarbon, chlorine-36 and helium-4. *Hydrogeology Journal*. **20** (2012) 1269-1294.
- [44] KULONGOSKI, J.T., HILTON, D.R., CRESSWELL, R.G., HOSTETTER, S., JACOBSON, G., Helium-4 characteristics of groundwaters from Central Australia: Comparative chronology with chlorine-36 and carbon-14 dating techniques. *Journal of Hydrology*. **348** (2008) 176-194.
- [45] MATSUMOTO, T., ZOUARI, K., TRABELSI, R., HILLEGONDS, D., JIANG, W., LU, Z.-T., MUELLER, P., ZAPPALA, J.C., ARAGUÁS ARAGUÁS, L.J., ROMEO, N., AGOUN, A., Krypton-81 dating of the deep Continental Intercalaire aquifer with implications for chlorine-36 dating. *Earth and Planetary Science Letters*. **535** (2020) 116120.
- [46] TORGERSEN, T., IVEY, G.N., Helium accumulation in groundwater. II: A model for the accumulation of the crustal ^4He degassing flux. *Geochimica et Cosmochimica Acta*. **49** (1985) 2445-2452.
- [47] BRENNWALD, M.S., SCHMIDT, M., OSER, J., KIPFER, R., A Portable and Autonomous Mass Spectrometric System for On-Site Environmental Gas Analysis. *Environmental Science & Technology*. **50** (2016) 13455-13463.
- [48] NAKATA, K., HASEGAWA, T., OHTA, T., JIANG, W., LU, Z.-T., MIYAKAWA, K., Method for ^{81}Kr Analysis and its Application to Deep Groundwater, in Japanese Association of Groundwater Hydrology Fall Meeting. (2022).
- [49] VALET, J.-P., MEYNADIER, L., GUYODO, Y., Geomagnetic dipole strength and reversal rate over the past two million years. *Nature*. **435** (2005) 802-805.

- [50] ZAPPALA, J.C., BAGGENSTOS, D., GERBER, C., JIANG, W., KENNEDY, B.M., LU, Z.-T., MASARIK, J., MUELLER, P., PURTSCHERT, R., VISSER, A., Atmospheric ^{81}Kr as an Integrator of Cosmic-Ray Flux on the Hundred-Thousand-Year Time Scale. *Geophysical Research Letters*. **47** (2020) e2019GL086381.
- [51] FELDMAN, G.J., COUSINS, R.D., Unified approach to the classical statistical analysis of small signals. *Physical Review D*. **57** (1998) 3873-3889.

LIST OF ABBREVIATIONS

| | |
|-------|--|
| AC | Activated Charcoal |
| ATTA | Atom Trap Trace Analysis |
| CRP | Coordinated Research Project |
| EDGAR | Extraction of Dissolved Gases for Analysis of Radiokrypton |
| GC | Gas Chromatography |
| IAEA | International Atomic Energy Agency |
| IHL | Isotope Hydrology Laboratory (IHL) |
| MFC | Mass Flow Controller |
| QMS | Quadrupole Mass Spectrometer |
| STP | Standard Temperature and Pressure |
| USTC | University of Science and Technology of China |

CONTRIBUTORS TO DRAFTING AND REVIEW

| | |
|-----------------|--|
| Ezaki, S. | Secretariat of Infrastructure and Environment of the State of São Paulo, Brazil |
| Gerber, C. | Commonwealth Scientific and Industrial Research Organisation, Australia |
| Jiang, W. | University of Science and Technology of China, China |
| Kaup, E. | Tallinn University of Technology, Estonia |
| Lu, Z-T. | University of Science and Technology of China, China |
| Mabry, J. | International Atomic Energy Agency |
| Martínez, D.E. | Universidad Nacional de Mar del Plata, Argentina |
| Matsumoto, T. | International Atomic Energy Agency |
| Mavidanam, S.R. | National Institute of Hydrology, India |
| Moulla, A.S. | Algiers Nuclear Research Centre, Algeria |
| Nakata, K. | Central Research Institute of Electric Power Industry, Japan |
| Nicolo, R. | International Atomic Energy Agency |
| Ouda, B | Centre National de l'Énergie, des Sciences et des Techniques Nucléaires, Morocco |
| Palcsu, L. | Hungarian Academy of Sciences, Hungary |
| Pinti, D.L | Geotop Research Center/Universite du Quebec a Montreal, Canada |
| Pitterbusch, F. | University of Science and Technology of China, China |
| Rashed, T. | Kuwait Institute for Scientific Research, Kuwait |
| Roland, B. | Federal Institute for Geosciences and Natural Resources, Germany |
| Saadi, R | Centre National de l'Énergie, des Sciences et des Techniques Nucléaires, Morocco |
| Trabelsi, R. | National School of Engineers of Sfax, Tunisia |
| Vaikmäe, R. | Tallinn University of Technology, Estonia |
| Wei, W. | Chinese Academy of Geological Sciences, China |

Yang, G. University of Science and Technology of China, China

Zouari, K Ecole Nationale d'Ingénieurs de Sfax, Tunisia

Research Coordination Meetings

Vienna, Austria: 8 – 11 November 2022, 2 – 6 December 2019, 11 – 14 June 2018

Consultant Meeting

Vienna, Austria: 23 – 26 April 2019



IAEA

International Atomic Energy Agency

No. 27

ORDERING LOCALLY

IAEA priced publications may be purchased from the sources listed below or from major local booksellers.

Orders for unpriced publications should be made directly to the IAEA. The contact details are given at the end of this list.

NORTH AMERICA

Bernan / Rowman & Littlefield

15250 NBN Way, Blue Ridge Summit, PA 17214, USA

Telephone: +1 800 462 6420 • Fax: +1 800 338 4550

Email: orders@rowman.com • Web site: www.rowman.com/bernan

REST OF WORLD

Please contact your preferred local supplier, or our lead distributor:

Eurospan

1 Bedford Row

London

WC1R 4BU

United Kingdom

Trade Orders and Enquiries:

Tel: +44 (0)1235 465576

Email: trade.orders@marston.co.uk

Individual Customers:

Tel: +44 (0)1235 465577

Email: direct.orders@marston.co.uk

www.eurospanbookstore.com/iaea

For further information:

Tel. +44 (0) 207 240 0856

Email: info@eurospan.co.uk

www.eurospan.co.uk

Orders for both priced and unpriced publications may be addressed directly to:

Marketing and Sales Unit

International Atomic Energy Agency

Vienna International Centre, PO Box 100, 1400 Vienna, Austria

Telephone: +43 1 2600 22529 or 22530 • Fax: +43 1 26007 22529

Email: sales.publications@iaea.org • Web site: www.iaea.org/publications

