

Nagra

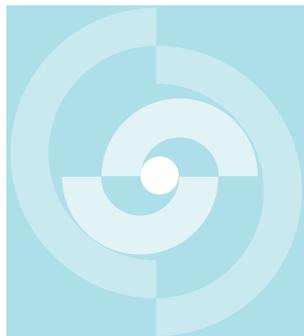
Nationale
Genossenschaft
für die Lagerung
radioaktiver Abfälle

Cédra

Société coopérative
nationale
pour l'entreposage
de déchets radioactifs

Cisra

Società cooperativa
nazionale
per l'immagazzinamento
di scorie radioattive



TECHNICAL REPORT 90-01

GRIMSEL TEST SITE

**GRIMSEL COLLOID EXERCISE:
AN INTERNATIONAL INTERCOMPARISON
EXERCISE ON THE SAMPLING AND
CHARACTERISATION OF GROUNDWATER
COLLOIDS**

JANUARY 1990

Organised by the Paul Scherrer Institute (PSI/CH),

co-organised by the National Cooperative for the Storage of Radioactive Waste (NAGRA/CH) and the Commission of the European Community (DGXII/EC).

C. DEGUELDRE (PSI)

as exercise manager and main investigator,

G. LONGWORTH (UKNP), V. MOULIN (CEA),

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with the participation of: C. Ross (BGS), G. Bidoglio (JRC), A. Cremers (KUL), J. Kim (TUM), J. Pieri (UNAN), J. Ramsay (UKC), B. Salbu (UNOS), U. Vuorinen (VTT) as characterisation authors.

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FOREWORD

Concepts which foresee the disposal of radioactive waste in geological formations lay great weight on acquiring knowledge of the proposed host rock and the surrounding rock strata. For this reason, Nagra has, since May 1984, been operating the Grimsel Test Site which is situated at a depth of 450 m in the crystalline formation of the Aar Massif. The general objectives of the research being carried out in this system of test tunnels include, in particular

- the build-up of know-how in planning, performing and interpreting underground experiments in different scientific fields and
- the acquisition of practical experience in developing, testing and applying test equipment and measuring techniques.

The Test Site (GTS) is operated by Nagra. On the basis of a German-Swiss cooperation agreement, the various experiments are carried out by Nagra, the Federal Institute for Geoscience and Natural Resources (BGR) and the Research Centre for Environmental Sciences (GSF); the latter two bodies are supported in this venture by the German Federal Ministry for Research and Technology (BMFT).

NTB 85-47 gives an overview of the GTS and a review of the status of the investigation programme as at August 1985.

This report was produced in accordance with the cooperation agreement between the three partners mentioned previously. The authors have presented their own opinions and conclusions, which do not necessarily coincide with those of Nagra, BGR or GSF.

VORWORT

Bei Konzepten, die die Endlagerung radioaktiver Abfälle in geologischen Formationen vorsehen, ist die Kenntnis des Wirtgesteins und der angrenzenden Gesteinsschichten von grundlegender Bedeutung. Die Nagra betreibt deshalb seit Mai 1984 das Felslabor Grimsel in 450 m Tiefe im Kristallin des Aarmassivs. Die generelle Zielsetzung für die Arbeiten in diesem System von Versuchsstollen umfasst insbesondere

- den Aufbau von Know-how in der Planung, Ausführung und Interpretation von Untergrundversuchen in verschiedenen Experimentierbereichen und
- den Erwerb praktischer Erfahrung in der Entwicklung, Erprobung und dem Einsatz von Testapparaturen und Messverfahren.

Das Felslabor (FLG) wird durch die Nagra betrieben. Die verschiedenen Untersuchungen werden aufgrund eines deutsch-schweizerischen Zusammenarbeitsvertrages durch die Nagra, die Bundesanstalt für Geowissenschaften und Rohstoffe (BGR) und die Gesellschaft für Strahlen- und Umweltforschung (GSF) durchgeführt, beide gefördert vom Deutschen Bundesministerium für Forschung und Technologie (BMFT).

Eine Uebersicht des FLG und die Zusammenfassungen der Untersuchungsprogramme sind mit Status August 1985 im NTB 85-47 enthalten.

Der vorliegende Bericht wurde im Rahmen der Zusammenarbeit zwischen den drei Partnern erstellt. Die Autoren haben ihre eigenen Ansichten und Schlussfolgerungen dargelegt. Diese müssen nicht unbedingt mit denjenigen der Nagra, BGR oder GSF übereinstimmen.

AVANT-PROPOS

La connaissance de la roche d'accueil et des couches rocheuses avoisinantes est d'importance fondamentale pour l'élaboration de concepts prévoyant le stockage de déchets radioactifs dans des formations géologiques. C'est pour cela que la Cédra exploite depuis mai 1984 le laboratoire souterrain du Grimsel à 450 m de profondeur dans le cristallin du massif de l'Aar. Les objectifs généraux des travaux menés dans ce complexe de galeries d'essais comprennent notamment:

- la constitution d'un savoir-faire dans la préparation, l'exécution et l'interprétation d'essais souterrains dans divers domaines et
- l'acquisition d'expérience pratique dans le développement, la mise à l'épreuve et l'engagement d'appareillages d'essais et de techniques de mesure.

Le laboratoire souterrain est exploité par la Cédra. Les différentes recherches sont réalisées dans le cadre d'un accord de collaboration germano-suisse par la Cédra, la "Bundesanstalt für Geowissenschaften und Rohstoffe" (BGR) et la "Gesellschaft für Strahlen- und Umweltforschung" (GSF), ces deux dernières instances étant soutenues par le Ministère allemand pour la recherche et la technologie (BMFT).

Un aperçu du laboratoire souterrain et un résumé des programmes de recherches apparaissent dans le rapport NTB 85-47 d'août 1985.

Le présent rapport a été élaboré dans le cadre de la collaboration entre les trois partenaires. Les auteurs ont présenté leurs vues et conclusions personnelles. Celles-ci ne doivent pas forcément correspondre à celles de la Cédra, de la BGR et de la GSF.



GRIMSEL-GEBIET

Blick nach Westen

- 1 Felslabor
- 2 Juchlistock
- 3 Räterichsbodensee
- 4 Grimselsee
- 5 Rhonetal

GRIMSEL AREA

View looking West

- 1 Test Site
- 2 Juchlistock
- 3 Lake Raeterichsboden
- 4 Lake Grimsel
- 5 Rhone Valley

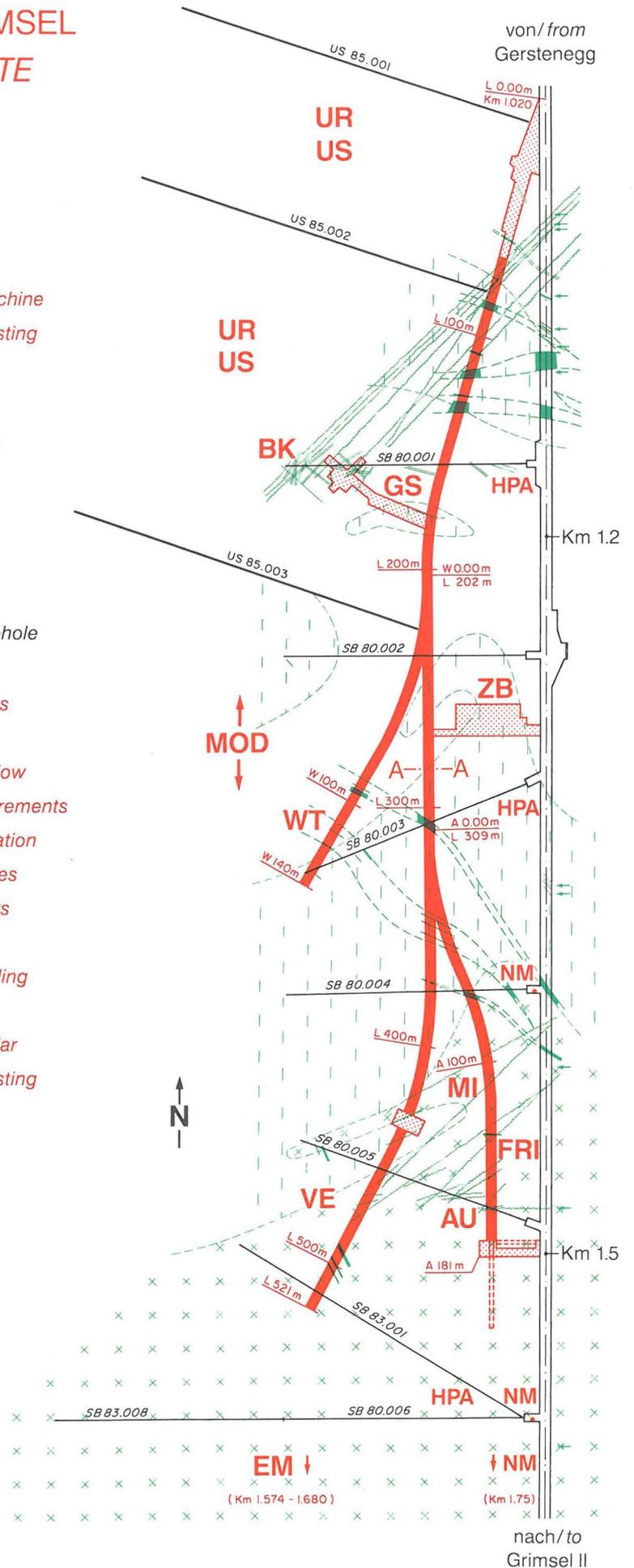
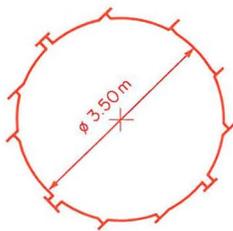
FLG FELSLABOR GRIMSEL
GTS GRIMSEL TEST SITE

Situation



- Zugangsstollen/ Access tunnel
- Fräsvortrieb/ by tunnel boring machine
- Sprengvortrieb/ excavated by blasting
- Zentraler Aaregranit ZAGR
Central Aaregranite CAGR
- Biotitreicher ZAGR
CAGR with high content of biotite
- Grimsel-Granodiorit
Grimsel-Granodiorite
- Scherzone/ Shear zone
- Lamprophyr/ Lamprophyre
- Wasserzutritt/ Water inflow
- Sondierbohrung/ Exploratory borehole
- US Bohrung/ US borehole
- ZB Zentraler Bereich/ Central facilities
- AU Auflockerung/ Excavation effects
- BK Bohrlochkranz/ Fracture system flow
- EM El.magn. HF-Messungen/ -measurements
- FRI Klufftzone/ Fracture zone investigation
- GS Gebirgsspannungen/ Rock stresses
- HPA Hydr. Parameter/ Hydr. parameters
- MI Migration/ Migration
- MOD Hydrodyn. Modellierung/ H. modeling
- NM Neigungsmesser/ Tiltmeters
- UR Untertageradar/ Underground radar
- US Seismik/ Underground seismic testing
- VE Ventilationstest/ Ventilation test
- WT Wärmeversuch/ Heat test

A — A Schnitt/ Section



EXECUTIVE SUMMARY

The Grimsel Colloid Exercise was an intercomparison project which consisted of an in-situ sampling phase followed by a colloid characterisation step. The goal of this benchmark exercise, which involved 12 laboratories, was to evaluate both sampling and characterisation techniques with emphasis on determining the colloid size distribution.

The sampling phase took place at the Grimsel Test Site between February 1 and 13, 1988 and the participating groups produced colloid samples using the following methods.

1. Cross-flow ultrafiltration with production of membranes loaded with colloids:

CEA performed the separation work using a 10 ml ultrafiltration cell (constant volume of water) and colloids were separated with membranes of different pore-size.

PSI used a pulsed diaultrafiltration rig in a plastic glove-bag (purged with N₂), working with 3 nm cut-off membranes and varying volume of water sample.

2. Tangential diaultrafiltration and production of colloid concentrates:

UKNP produced concentrated colloid samples with a hollow fibre (2.1 nm pore-size) system after prefiltration (1 µm) and used a plastic glove-bag (purged with N₂) to dispense the samples.

AECL produced the concentrate with a flat membrane cassette (1.5 nm pore-size) with no prefiltration.

3. Filtrates produced by each group.

4. Unfiltered water (28 samples of 1 l) was also collected by PSI in glass bottles, under controlled anaerobic conditions, and by the other sampling groups in various plastic bottles.

All samples were shipped to CoCo Club members for subsequent characterisation, with emphasis on size distribution determination.

While shipping and storage may affect the colloid samples, as well as the composition of both unfiltered/filtered water and concentrate samples from this somewhat demineralized water, the major element composition of the fluid samples was comparable between groups. However, air contamination decreases the pH from 9.6 to about 8, while increasing the concentration of total inorganic carbon.

The exercise differentiates the colloid samples produced on site from those obtained after transfer of the fluid samples to the laboratories. The colloid concentration and size distribution was determined by scanning electron microscopy, gravimetry, chemical analysis of fluid samples after micro/ultrafiltration and by transmission single particle counting. The colloid concentration was also evaluated by transmission electron microscopy, static and dynamic light scattering and by laser-induced photoacoustic spectroscopy.

The concentration of colloids ($\varnothing > 10$ nm) in Grimsel water is measured to be around 10^{14} pt.l⁻¹ and for $\varnothing > 50$ nm about 10^{10} pt.l⁻¹, although reported concentrations range over one order of magnitude between groups and according to the characterisation technique used. Particles ($\varnothing > 450$ nm) measured with scanning electron microscopy, gravimetry and transmission single particle counting appear to be around $2 \cdot 10^7$ pt.l⁻¹. On a weight basis, the concentrations of colloids and particles are around 50 and 100 ppb respectively and the total particle and colloid concentration is 200 ± 100 ppb.

The colloids consist of silica, illite/muscovite, biotite, calcium silicates and organics. A population of about 10^6 bacteria per litre is also present. The particles are negatively charged in-situ.

The results are discussed on the basis of the detection limit, lateral resolution and counting conditions of the technique (precision) as well as sample preparation, artefact production and measurement optimisation (accuracy). A good agreement between size distribution results was obtained with electron microscopy, gravimetry and particle counting for the original samples.

The main recommendations are the need for in-situ sampling, tracking of artefact production (e.g. ion retention, aggregation ...) and identifying contamination sources during subsample production. The combination of different techniques is finally recommended in order to ensure that no interference affects colloid analysis.

ZUSAMMENFASSUNG

Die Grimsel-Kolloid-Uebung umfasste eine in-situ-Probenahme-phase, sowie die Charakterisierung der Proben. Das Ziel dieses Benchmark bestand in der Evaluation von Probenahme- und Charakterisierungstechniken, mit Hauptschwergewicht auf der Bestimmung von Kolloid-Grössenverteilungen. Insgesamt waren 12 verschiedene Laboratorien an diesem Test beteiligt. Die Probenahme-phase fand vom 1.- 13. Februar 1988 im Felslabor Grimsel statt. Dabei wurden folgende Methoden verwendet:

1. Die Cross-flow Ultrafiltration liefert mit Kolloiden beladene Membranenfilter:

CEA: die Trennung wurde mittels einer 10 ml Ultrafiltrationzelle durchgeführt (konstantes Probenvolumen); Auftrennung der Kolloide durch Verwendung von Membranfiltern verschiedener Porengrössen.

PSI: Trennung mit Hilfe der Pulsed Diaultrafiltrationzelle unter Variation des Probenvolumens (Arbeit unter N_2 -Atmosphäre in einem Handschuhsack). Es wurden 3 nm cut-off-Membranen verwendet.

2. Die tangentielle Diaultrafiltration liefert Kolloidkonzentrate:

UKNP: Produktion von Konzentraten mittels Hohlfaser-System (2,1 nm Porengrösse), nach Vorfiltration (1 μ m); Verarbeitung der Proben unter N_2 -Atmosphäre.

AECL: Herstellung eines Konzentrates mittels einer Flachmembrankassette (1,5 nm Porengrösse) ohne Vorfiltration.

3. Filtration: durch alle beteiligten Gruppen wurden Filtrate hergestellt.

4. Die PSI Gruppe sammelte ausserdem unfiltrierte Wasserproben (28 zu je 1 l) in Glasflaschen unter kontrollierter O_2 -freier Atmosphäre. Die anderen Gruppen sammelten analoge Proben unter Verwendung verschiedener Plastikbehälter.

Alle Proben wurden gemäss den Richtlinien des CoCo-Club für die Charakterisierung von Kolloiden in Hinsicht auf deren Grössenverteilung transportiert.

Obwohl in den Kolloidproben Veränderungen durch Transport und Lagerung auftreten können und zwar sowohl in filtrierten und unfiltrierten Wasserproben, als auch in den Konzentraten, welche aus diesen mineralstoffarmen Wasserproben gewonnen wurden, war die chemische Zusammensetzung der Flüssigkeitsproben unter den Gruppen vergleichbar. Kontamination mit Luft führte jedoch zu einer pH-Senkung von 9,6 auf etwa 8,0, unter gleichzeitiger Zunahme des totalen anorganischen Kohlenstoffes.

Im Rahmen dieser Uebung wurden an Ort und Stelle produzierte (in-situ) Proben mit solchen verglichen, die erst nach dem Transport der Wasserproben in den Laboratorien aufgearbeitet wurden. Die Konzentration und Grössenverteilung der Kolloide wurden durch folgende Methoden bestimmt: Rasterelektronenmikroskopie, Gravimetrie, chemische Analyse der Wasserproben nach Micro/Ultrafiltration, Transmissionsteilchen-Zählung. Die Kolloidkonzentration wurde ferner mittels Transmissionselektronenmikroskopie, statischer und dynamischer Lichtstreuung und Laserinduzierter Photoakustischer Spektroskopie bestimmt.

Die Konzentration von Kolloiden ($\varnothing > 10$ nm) im Grimselwasser beträgt etwa 10^{14} pt.l⁻¹, und für $\varnothing > 50$ nm etwa 10^{10} pt.l⁻¹. Die Verwendung unterschiedlicher Charakterisierungstechniken ergab für die gemessenen Werte eine methodenspezifische Schwankungsbreite von c.a. einer Grössenordnung. Die beiden letzten Werte wurden mittels SEM bestimmt. Partikel mit $\varnothing > 450$ nm wurden mittels Rasterelektronenmikroskope sowie Gravimetrie und Transmissionsteilchen-Zählung bestimmt; es ergab sich ein Wert von $2 \cdot 10^7$ pt.l⁻¹. Gewichtsanteilmässig betragen die Konzentrationen von Kolloiden und Partikeln etwa 50 respektive 100 ppb. Die totale Kolloid- und Partikelkonzentration beträgt indessen 200 ± 100 ppb.

Die Kolloide bestehen aus Siliziumdioxid, Illit/Muskovit, Biotit, Kalziumsilikat und organischen Teilchen. Eine Population von etwa 10^6 Bakterien pro Liter ist ebenfalls vorhanden. Unter in situ Bedingungen tragen die Partikel negative Ladungen.

Die Resultate werden diskutiert in Hinsicht auf Nachweissgrenze, laterale Auflösung und quantitative Reproduzierbarkeit der Methoden (Präzision), als auch auf Effekte bei der Probeaufbereitung, auf Artefakte und auf Optimierung der Messbedingungen (Genauigkeit). Im Falle der Originalproben wurde für die Partikelgrössenverteilung eine gute Ueberstimmung zwischen den folgenden Methoden erzielt: Elektronenmikroskopie, Gravimetrie, sowie Partikelzählung.

Daraus ergeben sich folgende wesentliche Empfehlungen: die Probenahme muss in situ erfolgen, die Bildung von Artefakten muss genau untersucht werden (z.B. Retention von Ionen, Aggregation, usw), besondere Aufmerksamkeit ist Kontaminationsquellen bei der Probeaufbereitung zu schenken. Die Kombination verschiedener Techniken wird empfohlen, um Störeffekte bei der Kolloidanalyse möglichst auszuschalten.

RESUME

L'Exercice des Colloïdes du Grimsel est un projet de comparaison qui consistait en une phase d'échantillonnage in-situ suivie d'une étape de caractérisation. Le but de ce benchmark, qui impliquait 12 laboratoires, est d'évaluer les techniques d'échantillonnage et de caractérisation avec une attention particulière pour la distribution de taille des colloïdes.

La phase d'échantillonnage a eu lieu au Laboratoire Souterrain du Grimsel entre les 1^{er} et 13 février 1988 et les groupes y participant ont produit des échantillons de colloïdes en appliquant les méthodes suivantes:

1. Ultrafiltration à flux transversal avec production de membranes chargées de colloïdes:

Le CEA réalisant le travail de séparation en utilisant une cellule de 10 ml (volume d'eau constant), les colloïdes étant séparés à l'aide de membranes de différents diamètres de pore.

Le PSI utilisant son système de diaultrafiltration à impulsion dans un sac à gant (purgé à l'azote) travaillant avec des membranes de 3 nm de coupe et en faisant varier le volume de l'échantillon d'eau.

2. Ultrafiltration à flux tangentiel avec production de concentrés de colloïdes:

L'UKNP produisant des échantillons de concentré de colloïdes avec un système à fibres creuses (coupe 2,1 nm) après préfiltration (1 µm) et en utilisant un sac à gant (purgé à l'azote) pour répartir les échantillons.

L'AECL produisant ses concentrés à l'aide d'un système à cassette de membranes plates (de 1,5 nm de coupe) sans préfiltration.

3. Des filtrats produits par chaque groupe.

4. De l'eau non-filtrée (28 échantillons de 1 l) était également collectée sous atmosphère non-oxygène en bouteille de verre par le PSI et en diverses bouteilles en plastique par les autres groupes.

Tous les échantillons ont été expédiés, selon le protocole arrêté au CoCo Club, pour caractérisation, avec une attention particulière pour la distribution de taille.

Alors que le transport et l'entreposage peuvent affecter les échantillons de colloïdes ainsi que la composition des phases non-filtrées, filtrées et concentrées de cette eau plutôt déminéralisée, la composition des éléments majeurs des échantillons fluides était comparable d'un groupe à l'autre. L'effet de la contamination de l'air diminuait cependant le pH de 9,6 à 8, augmentant par la même occasion la concentration en carbone inorganique total.

L'exercice différencie les échantillons de colloïdes produits au site de ceux obtenus après transfert des échantillons fluides au laboratoire de caractérisation. Les concentrations et distributions de taille des colloïdes ont été obtenues par microscopie électronique à balayage, gravimétrie, et analyse chimique des échantillons fluides après micro/ultrafiltration, comptage de particule par transmission. La concentration en colloïde était également évaluée par microscopie électronique à transmission, diffusion statique ou dynamique de lumière et par spectroscopie laser photoacoustique.

Dans l'eau du Grimsel, la concentration en colloïde ($\varnothing > 10$ nm) est approximativement de 10^{14} pt.l⁻¹ et pour $\varnothing > 50$ nm d'environ 10^{10} pt.l⁻¹, quoique les concentrations reportées varient d'un ordre de grandeur selon les groupes et techniques de caractérisation utilisées. Les particules ($\varnothing > 450$ nm) mesurées par microscopie électronique, gravimétrie et comptage de particule ont une concentration de l'ordre de $2 \cdot 10^7$ pt.l⁻¹. En terme de masse, les concentrations respectives en colloïde et particule sont de 50 et 100 ppb respectivement et la concentration totale est de 200 ± 100 ppb.

Les colloïdes sont constitués de silice, illite/muscovite, biotite, silicate de calcium et de matière organique. Une population d'environ 10^6 bactéries par litre est aussi présente. Les particules sont chargées négativement in-situ.

Ces résultats sont discutés sur base des limites de détection, résolutions latérales et conditions de comptage des techniques (précision) aussi bien que de la préparation des échantillons, de la production d'artéfacts et de l'optimisation des mesures (exactitude). Une bonne cohérence est remarquée lorsque les résultats de microscopie électronique, gravimétrie et comptage de particule sont comparés pour les échantillons originaux.

Les principales recommandations sont: le besoin d'échantillonnage in-situ, de recherche de l'origine de la production potentielle d'artéfacts (p.e. rétention d'ion, aggrégation, ...) et de source de contamination durant la production des échantillons. La combinaison de technique est finalement recommandée en vue de contrôler qu'aucune interférence n'affecte l'analyse des colloïdes.

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Table 1: List of participants in the Grimsel Colloid Exercise.

Abbrev.	Working laboratory	Activity
-----	-----	-----
AECL:	Atomic Energy of Canada Ltd, Pinawa (C).	Sampling
BGS :	British Geological Survey, Keyworth (UK).	Characterisation
CEA :	Commissariat à l'Energie Atomique, Fontenay, (F).	Sampling
JRC :	Joint Research Centre, Ispra (EC).	Characterisation
KUL :	Katholieke Universiteit Leuven, Heverlee (B).	Characterisation
PSI :	Paul Scherrer Institut, Villigen (CH).	Sampling
TUM :	Technische Universitaet Muenchen, Inst. Radiochem, (FRG).	Characterisation
UKC :	Harwell Laboratories, Chemistry Division, (UK).	Characterisation
UKNP:	Harwell Laboratories, Nuclear Physics Division (UK).	Sampling
UNAN:	Université de Nantes, Lab. Radiobiochimie, Nantes (F).	Characterisation
UNOS:	Agricultural University of Norway, Isotope Laborat. (N).	Characterisation
VTT :	Technical Research Centre of Finland, Espoo (SF).	Characterisation

Remarks: the groups involved in the sampling (subsample preparation) were also involved in the characterisation. Subsample preparation and characterisation measurements were carried out in duplicate wherever possible.

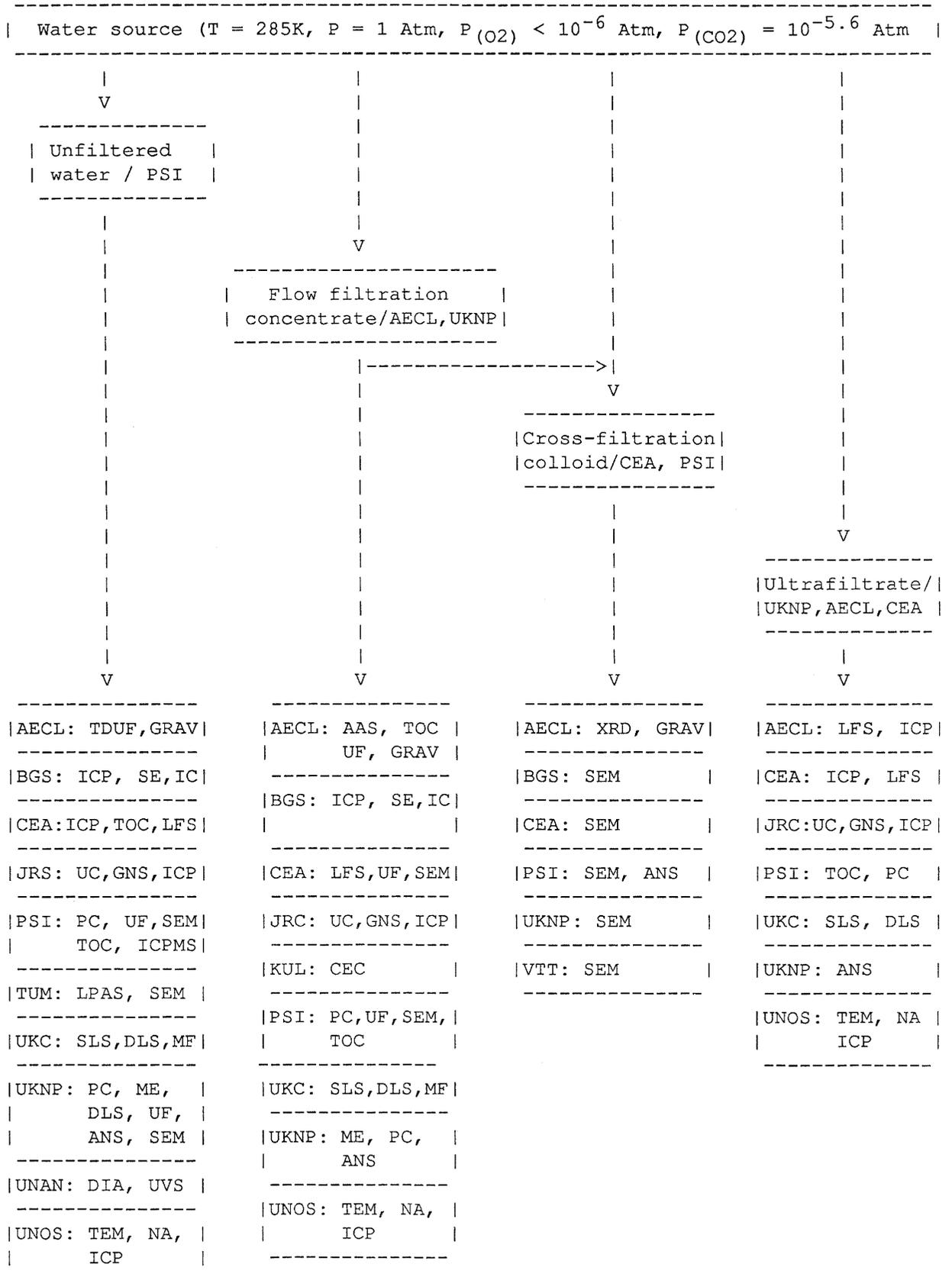
1 INTRODUCTION

Natural colloids have been identified as potentially important factors in repository safety analyses [GEW85,AVO84,MCC89] and several groups are currently developing techniques for sampling, characterising and quantifying colloids in relevant groundwater systems. A range of different approaches to colloid sampling has been tested, involving various techniques for extracting groundwater followed by, for example, ultracentrifugation, ultrafiltration or dialysis. However, there has, as yet, been little effort towards comparing the results obtained using different approaches at a single site. With increasing amounts of colloid data becoming available, it was important to launch inter-laboratory sampling and characterisation campaigns in order to allow data from different sources to be integrated and possible sampling artefacts to be identified for each technique.

Following a suggestion made at the Natural Analogue Working Group Meeting of the EC at Interlaken, Switzerland in June 1986 [MCK86], the EC agreed, in principle, to coordinate such a colloid study. This study was seen as parallel to the work of the MIRAGE II natural organo-complex intercomparison exercise and was integrated into the framework of the colloids and complexants Club (CoCo Club) which had been established at an earlier date. Two sampling sites were identified and the first EC CoCo Club meeting (Brussels, July'86) discussed colloid sampling in water from sites at South Terras (UK) and Grimsel (CH). At the second CoCo Club meeting (Brussels, September'86) another British water (Markham Clinton) was included in the list. It was also decided to include Ispra water (I) to allow the colloid content in these three waters to be measured by laser photoacoustic spectroscopy (TUM; abbreviations in section 10) and the water with the highest colloid content to be identified. At the 3rd CoCo Club meeting (Brussels, November'86) an additional water (Gorleben) was presented. The measured colloid concentration was Ispra \approx Markham < Grimsel < Gorleben. For practical reasons, the first colloid benchmark exercise took place at Markham (UK) in January'87. BGS organised the exercise; the sampling was performed by UKNP and PSI and the characterisation campaign was carried out by UKNP, PSI, CEA, BGS and JRC. At the 4th CoCo Club meeting (Munich, April'87) the research groups reported low colloid concentrations and difficulties in comparing results. It was thus decided to investigate Grimsel colloids as well as those from Gorleben. In the meantime, Gorleben water samples in contact with the local rock were shipped to the laboratories involved in the Gorleben exercise. At the 5th CoCo Club meeting (Ispra, October'87), TUM checked that the groups involved in the Gorleben experiment had received the German samples and the status of the Grimsel colloid sampling and characterisation study was presented on the basis of the PSI studies [DEG87a, DEG87b]. After the 5th CoCo Club meeting and an internal NAGRA/PSI discussion, priority was given to the sampling phase of the Grimsel Colloid Exercise which was to be held in February'88.

In the Grimsel Colloid Exercise, the water extraction and sampling steps are the key procedures to be evaluated, along with the characterisation step itself. It should not be considered premature to compare sampling methods before intercalibration of analytical techniques. Preparation of "standard colloid" solutions which are "stable", representative of natural colloids and applicable in all analyses (ranging from mineralogy to radiochemistry) is considered to be beyond present resources. The calibration of specific analytical techniques [BAR89] (e.g. organic characterisation) using standard colloids is thus inherently restricted. However, model colloids are occasionally used to calibrate particular techniques [LET89] used for characterisation.

Table 2: Grimsel Colloid Exercise sampling and characterisation scheme.
 (See section 10 for abbreviations)



The Grimsel Test Site (GTS) and, more precisely, the water from the fractured granite of the migration zone (for details, see Figure 1) which flows from an encapsulated source (termed the kalotte), was selected for the following reasons.

- The temperature and pressure conditions in-situ (in the rock) are representative of those in the rock laboratory (GTS) and are of general interest.
- The anoxic groundwater has a steady flow-rate and sampling at the kalotte can be carried out from an outlet without a sedimentation trap.
- The average colloid concentration is greater than in the Markham water [ROS87].
- The contamination risk is small. The water is collected without borehole liners or packers. A teflon cup encapsulates the water source with flow occurring through tubes of specially selected material.
- The composition of the Grimsel groundwater is very stable and its chemistry has shown no significant seasonal variation over the last two years [BAJ87].
- Both organic and inorganic colloids are present.
- The site is well characterised and has been selected for a radionuclide migration experiment [MCK88].
- Studies on water chemistry and colloids already exist and show that, as with most groundwater, the Grimsel water is not in equilibrium with air. Water contact with air (CO_2) is clearly indicated by a drop in pH but, in this case, there is no calcite precipitation (minimising artefact generation) [DEG87a].
- Access to the GTS is relatively easy (even in difficult weather conditions) and the facilities and materials available on site allow the field work to be performed in a comfortable environment.

The colloid sampling was based on both direct water sampling and various concentration/separation schemes performed in duplicate. The sampling phase was followed by a characterisation campaign subsequent to a shipping/storage transition phase. The second step was initiated as soon as feasible after receiving the samples. These phases are sketched in Table 2 together with the participant groups (see Table 1) and the analytical techniques used.

2 DESCRIPTION OF THE GEOLOGICAL AND SAMPLING ENVIRONMENT

The Aar Massif, in which the Grimsel Test Site (GTS) is situated (Figure 1), has been subjected to several periods of tectonic activity and associated stress release has resulted in an ENE-WSW-striking, 70 - 80° dipping fracture system. Along with a series of aplitic dykes, these fractures act as the main control on groundwater flow in the granite [NAG85]. The fracture chosen for the colloid intercomparison exercise has been selected for a radionuclide migration experiment [HAD88,MCK88] and has therefore been extensively characterised. This fracture intersects the GTS drift almost perpendicularly and, mineralogically, is typical of the local "alpine" low temperature (or greenschist facies) mineral associations, with the infill material (so-called "mylonite") containing quartz, chlorite/smectite/illite, K-feldspar, albite, biotite, muscovite and epidote [MEY89]. The fracture is bordered by a 5 - 10 cm wide schistose margin which grades into the associated Grimsel granodiorite.

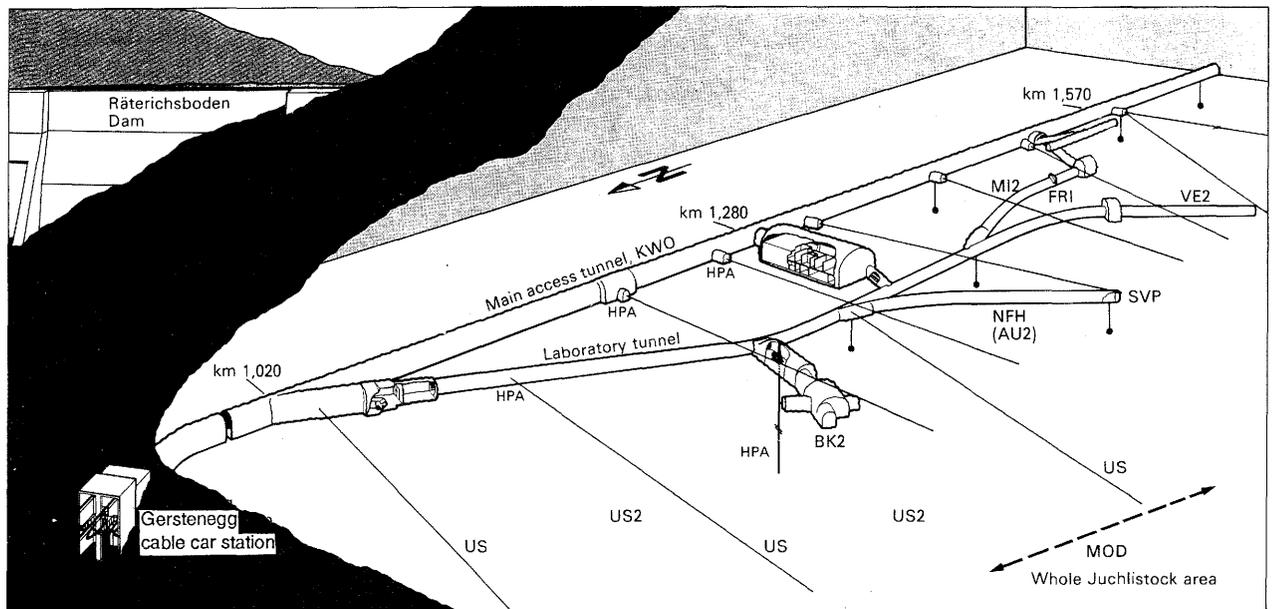
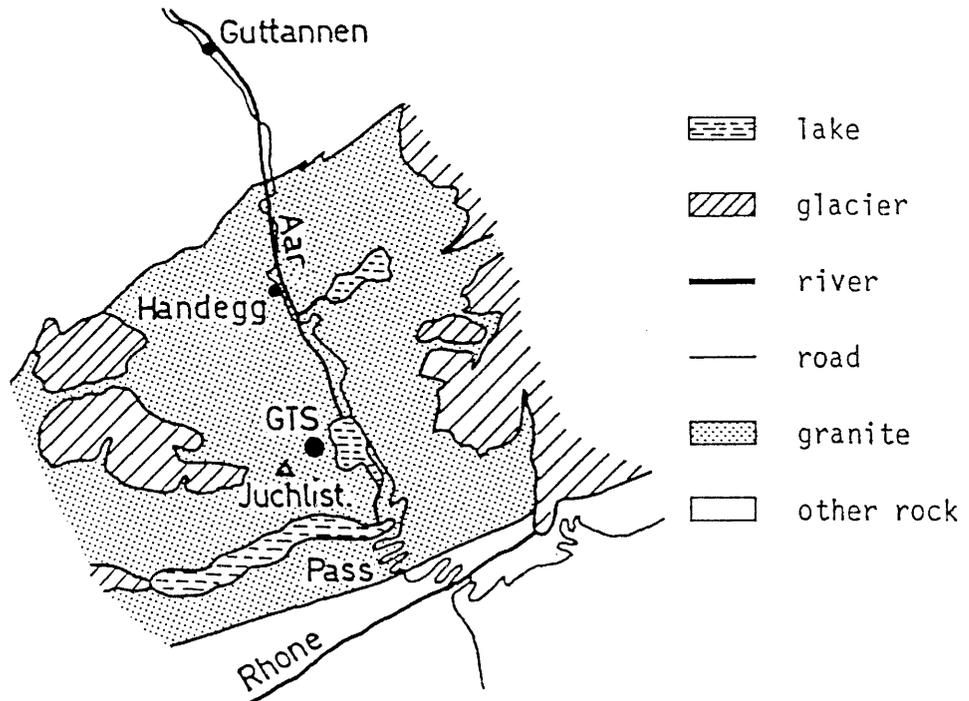
The water flowing in the mylonite of the migration zone can be collected at the wall of the drift with a teflon cup. The cup is pressed into a hollow in the granodiorite wall by a stainless steel brace screwed into the rock, and the seal maintained by a series of teflon O-rings. The system was installed in early November'87 and allowed to flush until February'88. In the meantime, a plastic sheet was placed over the whole zone, sealed to the rock face and the internal space flushed with nitrogen. The water, which has a constant temperature of 285 K and a flow-rate of 180(±20) ml.min⁻¹, was collected from either an upper or lower outlet after passing through PVDF tubes. The conducting tubes were washed with alcohol and seven times with ultrapure water before being attached to the kalotte 5 days before sampling.

The major element chemistry of the water remained effectively constant over the twenty months previous to the exercise. Similarly, and for the same period of time, there has been no observed change in the colloid concentration (around 10¹⁰ part.l⁻¹ [DEG89]).

The gases used for the sampling phase of the exercise were nitrogen quality 5.5 (Industriegase Werk Duisburg) and quality 6.0 (Air Liquide). [O₂] and [CO₂] were <0.5 and <0.1 vpm for the 5.5 nitrogen and <0.1 and <0.1 vpm for the 6.0 nitrogen respectively.

The continuous measurements of water pH, electrical conductivity, temperature and dissolved oxygen concentration were carried out on-line with three separate probes. A combined Wissenschaftlich-Technische Werkstaetten E-50 pH-electrode with a TFK-530 temperature sensor recorded the pH, a conductimeter with integrated temperature sensor measured the electrical conductivity and the dissolved oxygen content was measured with an oxygen electrode (a membrane-covered amperometric electrode of the Clark type). The pH-electrode was calibrated with Merck buffer solutions of pH 7.00 and pH 9.00, the conductivity electrode was calibrated with KCl solutions of differing concentrations and the oxygen electrode was calibrated by measuring air-saturated water in the Oxi Cal R calibration vessel. The electrodes were fitted into a flow-through cell which was placed on-line after the colloid sampling equipment. Data was collected by an Eto Denki Thermodac-32 logger and, for the duration of the sampling phase of the exercise, no significant fluctuations were detected.

Oxygen levels in the sampling systems were measured with a Teledyne System 311-1 portable oxygen analyser (four scales 0-10, 0-100, 0-1000, 0-10000 ppm) drawing gas directly from the colloid sampling cell or from the glove-bag. The cell is operable from 273 to 323 K with an accuracy of ±2% full scale deflection over the range observed in the PSI glove-bag.



US	Exploration borehole	FRI	Fracture zone investigation	NFH	Near-field hydraulics
US	US-borehole	HPA	Hydraulic parameters	SVP	Predict. ahead of tunnel face
AU2	Excavation effects	MI2	Migration test	US2	Underground seismics
BK2	Fracture system flow test	MOD	Hydrodynamic modelling	VE2	Ventilation test

Figure 1: Grimsel Test Site: location, geological map and site profile.

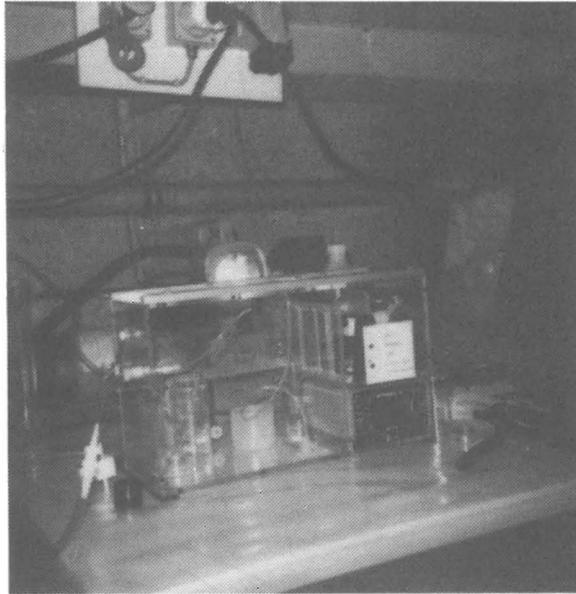


Figure 2: CEA filtration rig and sample shipping scheme.

On-site production :

Sample	pore-size/nm	membrane type	laboratories
CEA1	3	Amicon XM50 polyacrylamide	CEA, PSI, BGS, UKNP
CEA2	15	Amicon XM300 polyacrylamide	CEA, PSI, BGS, AECL
CEA3	15	Amicon XM300 polyacrylamide	CEA, PSI, BGS, UNOS
CEA4	220	Millipore cellulose esters	CEA, PSI, BGS, UKNP
CEA5	100	Millipore cellulose esters	CEA, PSI
CEA6	450	Millipore cellulose esters	CEA, PSI

In-laboratory production:

Subsamples for CEA use only

Conditions: constant volume : 20 ml
 constant stirring: 200 rpm
 total active area: 3.5 cm²
 quartered membrane.

3 COLLOID SAMPLING PROCEDURE ON SITE

Since the transfer of sophisticated characterisation apparatus to the site is difficult or impractical, separation units have been used for fractionation/separation in the field. For the Grimsel Colloid Exercise, separation by cross-flow micro/ultrafiltration and fractionation/concentration by tangential filtration were performed [DEG88].

3.1 COLLOID SAMPLING BY CROSS-FLOW FILTRATION

Colloid sampling and characterisation can be carried out by combining cross-flow filtration and scanning electron microscopy investigations. For the exercise, CEA and PSI performed the sampling phase by carrying out the filtration with constant volume but varying pore-size (CEA) and, by way of a complementary exercise, with constant pore-size but changing volume of filtered water from one ultrafiltration to another (PSI).

3.1.1 CEA SAMPLING

The approach used here was micro/ultrafiltration onto a flat membrane (of differing pore-size) in a cell set into a box which was subdivided as follows:

- section for the ultrafiltration cell with a magnetic stirrer and nitrogen input,
- section for the water sampling, the manipulation of membranes and ultrafiltrate collection with an argon input (inert gas for the box) and a nitrogen input (to purge the water in the glass sampling cell and the ultrafiltrates).

This box also prevents dust contamination. All materials were cleaned with alcohol and rinsed with distilled water before use. The ultrafiltration materials (cell, membrane, tubing) were Amicon (except for the 220 nm membrane) and consisted of a 10 ml cell with a membrane of 25 mm diameter. The membranes were a Diaflo XM50 (3 nm), a Diaflo XM300 (15 nm) and a Millipore (pore-size 220 nm). The membranes of 3.5 cm² active area were washed with Millipore water (1 h minimum) before use. The water was collected in a glass bottle and flushed with quality 6.0 nitrogen to avoid contamination with air. The injection of the water into the ultrafiltration cell was performed manually with an Eppendorf pipette (10 ml).

The concentration was carried out as follows. In order to obtain enough colloidal material for SEM examination, 20 ml of water was ultrafiltered under a pressure of 1 bar of nitrogen (quality 6.0) with continual stirring. After concentration, the membranes were dried under nitrogen in the cell, placed in a plastic box and transferred to a desiccator under vacuum to finish the drying. The plastic box containing the membrane was then sealed in a plastic vial to minimise contamination. In addition, ultrafiltrates and groundwater were sampled for total organic carbon, U and major ion analysis. The CEA production unit and sample shipping scheme is presented in Figure 2.

3.1.2 PSI SAMPLING

The separation work was carried out with the pulsed diaultrafiltration unit described in detail elsewhere [DEG87a]. The rig containing the ultrafiltration cell (1st barrier, [O₂] < 1 ppm) was installed in a plastic glove-bag (2nd barrier) purged with N₂ in order to maintain the oxygen concentration at about 500 ppm. The water flowed directly from the kalotte into an 800 ml reservoir



Figure 3: PSI pulsed diaultrafiltration rig in the glove-bag and sample shipping scheme.

On-site production

Sample	V/ml	membrane type (const.pore 3nm)	Laboratory
PSI1	76	Amicon XM50 polyacrylamide	PSI, BGS, CEA, AECL
PSI2	44	Amicon XM50 polyacrylamide	PSI, BGS, UNOS, UKNP
PSI3	46	Amicon XM50 polyacrylamide	PSI, BGS, CEA, AECL
PSI4	26	Amicon XM50 polyacrylamide	PSI, BGS, UNOS, UKNP
PSI5	150	Amicon XM50 polyacrylamide	PSI, BGS, VTT, PSI

In-laboratory production with concentrate and groundwater

Sample	V/ml	membrane type	Laboratory
PSI1'UKNP2	2	Amicon XM50 polyacrylamide	PSI, BGS, TUM, VTT
PSI2'AECL1	2	Amicon XM50 polyacrylamide	PSI, BGS, TUM, VTT
PSI1"	45	Amicon XM300 polyacrylamide	PSI, BGS, VTT, AECL
PSI2"	25	Amicon XM300 polyacrylamide	PSI, BGS, VTT, AECL
PSI3"	10	Amicon XM300 polyacrylamide	PSI, BGS, VTT, AECL
PSI4"	5	Amicon YC05 polysaccharide	PSI, BGS, VTT, TUM
PSI5"	20	Amicon PM10 polysulfone	PSI, BGS, VTT, TUM

Conditions: - no pretreatment
 - no stirring
 - active surface: 1.2 cm²

without pretreatment (no degassing or prefiltration). The sampling was performed on-line and the automatic injection of the water into the 6 ml mini-ultrafiltration cell required a small overpressure (< 0.1 bar) while the ultrafiltration was carried out under 1 bar of N_2 (quality 6.0). The membranes selected for this exercise were Amicon XM 50 (polyacrylamide, pore-size 3nm) which were soaked for at least 2 hours in Millipore water and then rinsed prior to placing them in the cell. The ultrafiltrations were performed to dryness and the dried membranes (vacuum, N_2) were quartered, encapsulated in small gold-coated plastic boxes (1st barrier) and placed in a larger box which was itself sealed in a small plastic bag (additional barrier) prior to being mailed to the characterisation laboratories. The PSI production unit and sample shipping scheme are depicted in Figure 3 .

3.2 CONCENTRATE PRODUCTION BY TANGENTIAL ULTRAFILTRATION

Colloid concentrate production was carried out in parallel with hollow fibre (UKNP) and flat membrane (AECL) systems. While AECL processed the water without prefiltration and with a 10,000 mwu (1.5 nm) cut-off [VIL88c], UKNP produced the concentrate (cut-off 30,000 mwu, 2.1 nm) after prefiltration (1 μ m) [IVA86].

3.2.1 UKNP SAMPLING

For the last two years, the Harwell laboratory has been using an ultrafiltration technique [IVA86] with hollow fibre cartridges with cut-offs of 30,000 mwu (2.1 nm) up to 100 nm. For the Grimsel exercise, the rig used consisted of:

- a prefiltration Gelman holder (plastic) containing a Nuclepore 1 μ m filter (polycarbonate, 1.7 m²)
- an Amicon CH2A ultrafiltration rig incorporating a peristaltic pump, a hollow fibre column (polysulfone membrane 30,000 mwu) and a two-litre reservoir (RA 2000).

The ultrafiltration rig was purged with N_2 and washed with Grimsel water for about 30 min. Prefiltered water filled the ultrafiltration cell and was circulated for 10 min in the system before being drained off and the cell refilled with N_2 and prefiltered water. During the concentration stage, the volume of the processed concentrate sample was kept constant by adjusting the pump speed and the back-pressure across the cartridge filter (1 bar). The water input (180 ± 20 ml.min⁻¹) and the ultrafiltrate output rates were thus kept equal. Some of the ultrafiltrate was collected aerobically for uranium series measurements.

On February 9, about 60 l of water were processed and, on completion of this concentration, 2 l of colloid concentrate were transferred anaerobically, using the rig peristaltic pump, to amber glass bottles (under N_2). The dispensing of the samples to the CoCo Club members was carried out in an N_2 -purged glove-bag (Aldrich, about 100 l) with an O_2 concentration of about 10,000 ppm in the bag atmosphere.

On February 10, the process was repeated for 90 l of Grimsel water, taking the precaution of purging the glove-bag six times with N_2 to reduce the oxygen level. The UKNP production unit and sample shipping scheme are presented in Figure 4.

3.2.2 AECL SAMPLING

Prior to colloid concentration, 50 l of Grimsel groundwater were collected in a polyethylene container filled with nitrogen. The 50 l collection vessel was evacuated and flushed with nitrogen four times before sample collection. Water was transferred from the kalotte to the sample vessel through a PVDF tube with no prefiltration. Nitrogen displaced by incoming water was able to escape from the sample container through a one-way valve. Groundwater which was used to

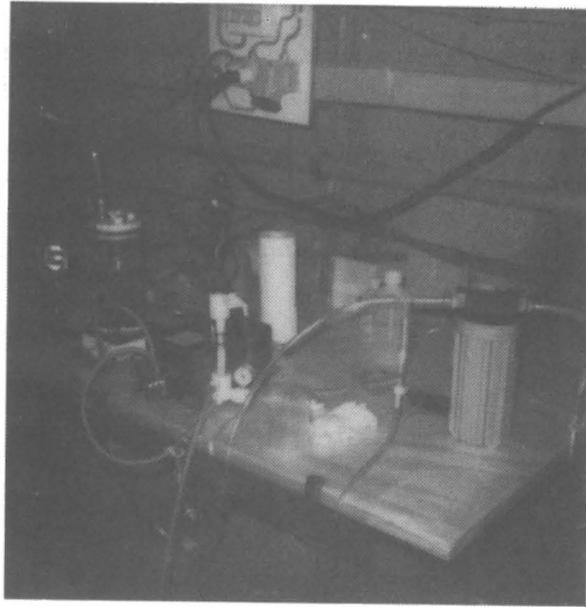


Figure 4: UKNP filtration system and sample shipping scheme.

Sample	concentration factor	V concentrate/ml	laboratory
UKNP1	28 X	250	CEA
		250	UKC
		250	JRC
		250	UNOS
		1000	UKNP
UKNP2	38 X	200	KUL
		250	PSI
		250	BGS
		250	AECL
		250	UKNP
		800	UKNP

Conditions:

- prefiltration: 1 μm Nuclepore filter
- ultrafiltration: 2.1 nm polysulfone hollow fibre
- prefilter ext. surface: 1.7 m^2
- hollow fibre surface: 600 cm^2
- pressure drop through UF: 1 bar
- UF flow in process: 10 l.h^{-1}

concentrate colloids for CoCo Club members was collected during the night of February 9. By the time sampling stopped next morning, about 150 l had flowed through the sample container.

Immediately after groundwater sampling had ceased, colloids were concentrated with the Pellicon tangential flow ultrafiltration system containing a 4,600 cm² polysulfone membrane with 1.5 nm cut-off (10,000 mwu). Water was pumped from the 50 l container to the filter membrane and back using a circuit isolated from the atmosphere. Before filtration, the ultrafiltration system (Pellicon) was flushed with 2 l of sample water which was then discarded. As filtered water was removed at a rate of 1 l.min⁻¹, colloids were concentrated in the 50 l container, where nitrogen replaced the volume of water removed. At the end of the filtration procedure, a 48 l sample had produced a 2.3 l colloid concentrate with particles larger than 1.5 nm. The pH of the filtered water remained 9.6 at the end of the procedure, indicating that no CO₂ contamination had taken place. The retentate was quickly transferred to sample bottles without the protection of a nitrogen atmosphere; this was not felt to be necessary for the following reasons:

1. once filtration is complete, the transfer of elements between the filtrate and retentate is not affected by exposure to the atmosphere,
2. oxidation can be a problem if Fe(II) species are present which can be oxidised to Fe hydroxide colloids. If the total Fe concentration is less than 20 ppb, with perhaps 0.01 ppb Fe(II), Fe oxidation should not affect the 10 ppm colloids which may be present in the retentate samples,
3. in-situ experiments have shown that the pH of Grimsel water does not change significantly within 20 minutes of standing open to the atmosphere (Figure 6). Hence, it was assumed that the CO₂ contamination should not affect the colloid samples during the transfer process.

The polyethylene bottles of concentrate were shipped to the CoCo Club members according to the scheme presented in Figure 5; this Figure also shows the AECL production unit.

3.3 UNFILTERED WATER SAMPLING

The water sampling was performed on February 12, in glass bottles as agreed by the CoCo Club. Thirty 1 l bottles were cleaned with alcohol, 0.1 M HNO₃ and 7 times with MilliQ water. The stoppers were sonically cleaned in MilliQ water prior to 5 rinses in this water. The bottles and stoppers were stored under a controlled atmosphere and irradiated with UV light for one week to remove as much bacterial contamination as possible.

The sampling material was placed in the PSI plastic glove-bag system and conditioned 6 times (vacuum + N₂ inflation). When filling the bottles, the oxygen concentration was maintained between 100 and 1,000 ppm. As a first step towards minimising water contamination, the sampling material was purged with nitrogen (quality 6.0); the oxygen concentration fluctuated around the 1 ppm level in the sampling vessel atmosphere. The bottles were filled at a water flow rate of 200 ml.min⁻¹. After capping, the filled bottles were transferred to a thermostatic box, covered with Grimsel water and transported to PSI where they were then placed in a plastic bag filled with nitrogen and sealed prior to shipping to the CoCo Club members involved in this exercise.

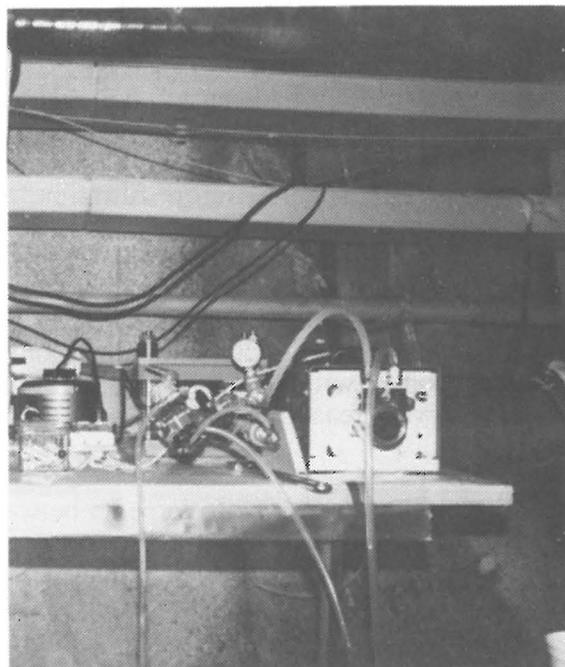


Figure 5: AECL ultrafiltration rig and sample shipping scheme.

On-site production of concentrate (AECLi) and of ultrafiltrate (AECLi'):

Sample	concentration factor	V concentrate / ml	Laboratory
AECL1	20.9 X	100	AECL
		100	BGS
		100	CEA
		100	JRC
		100	PSI
		100	UNOS
		100	UKC?
		100	each group
AECL'	-	100	
AECL2	48.0 X	600	AECL (GRAV)
		400	PSI
AECL3	384 X	200	KUL

In-laboratory sample production AECL4 (for AECL use only) with shipped groundwater.

Conditions:

- no prefiltration
- ultrafiltration: 1.5 nm polysulfone flat membrane
- membrane area: 4,600 cm²
- pressure drop through UF: 3 bars
- UF flow in process: 60 l.h⁻¹

4 SAMPLE SHIPPING AND STORAGE

After sample preparation at the GTS, the packaged samples (responsibility of sampling groups) were shipped to the various laboratories involved in the characterisation phase (see Table 1). In most of the laboratories, as in PSI, they were stored for a certain period prior to analysis. As the shipping conditions differed from one sample to another, and as these conditions were impossible to control, the characterisation phase was performed freely by each laboratory according to its own methodology and time-table. Prior to presenting the characterisation phase, it is useful to discuss potential sample alteration, artefact production and contamination of both colloid and fluid samples.

Colloids separated by cross-flow filtration are dried prior to transportation. Modification of their structure, morphologic appearance and chemical composition is possible. In addition, losses due to non-adhesion are possible, as well as contamination by dust or airborne particles. All these interferences can be estimated by investigating blanks, or by changing the filtration geometry (volume, membrane active area and the membrane material).

In the fluid samples (concentrate, unfiltered water), the risks of sample degradation are multiple and consist of potential contamination, aggregation, disaggregation and losses by sorption. With a concentration of, say, 10^{10} particles of about 100 nm diameter per litre, the total colloid surface for 1 litre is in the order of a square centimetre, which is at least two orders of magnitude smaller than the surface of the bottle containing the one litre sample. Hence, colloid losses by sorption onto the bottle and a colloid monolayer formation on the surface of the container is possible even if unlikely because of the high pH of the water which will tend to give a negative charge to both the colloid and the glass surfaces (colloids being composed mainly of clay, silica and organics). However, traces of iron hydroxide colloid could act as a cement and aggregate colloids locally. This hypothesis needs to be considered further. In addition, glass leaching (glass bottle) or monomer/low molecular mass polymer dissolution (plastic container) are potential artefact sources. Finally, various types of contamination are possible, for example bacterial (with subsequent proliferation), chemical (with CO_2 or O_2 from air) or with particles from the atmosphere in contact with the sample. These interferences could be evaluated by comparing blanks, filtrates or samples obtained by changing the enrichment factor (for chemical analysis) or by performing cross-flow filtration on site and in the laboratory. The effect of air contamination on the pH of the water sample is shown in Figure 6.

These potential artefacts are of great importance and are considered in more detail in the following discussion.

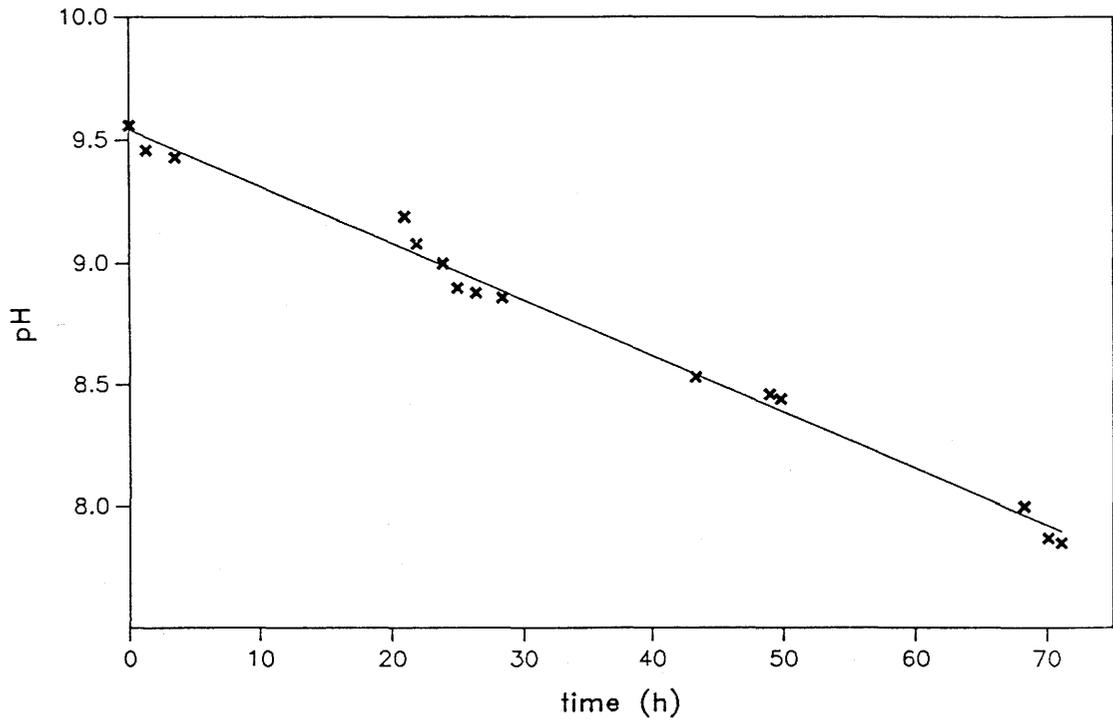


Figure 6: Effect of air contamination on the pH of the Grimsel water.
 Conditions: in-situ T and P, V = 200 ml, air contacted area: 50 cm².

5 CHARACTERISATION

Since, by definition, a colloidal solution is thermodynamically unstable, it is reasonable to distinguish results obtained with in-situ colloid sample preparation from those obtained by characterisation of the fluid sample after shipping and storage. For the water, only key parameters are measured on site i.e.: temperature: 285 K, conductivity: 106 mS.cm⁻¹, pH = 9.6 and [O₂].<100 ppb. Major and minor components are analysed after transfer of the water to the laboratory. Details of the analytical methodology and techniques are given in sections 5.2 and 5.3 .

In this study, colloids are defined restrictively as having a diameter ranging from 1 to 450 nm, while particles are defined as larger than 0.45 µm [BEN80]; the IUPAC colloid definition includes sizes ranging from 1 to 1,000 nm. Since the size distribution should be independent of the measuring technique (size class), the data are presented in terms of normalized concentration $\delta[\text{coll}]/\delta\phi$ the units being pt.l⁻¹.nm⁻¹ or g.l⁻¹.nm⁻¹, while the cumulative size distribution is given in pt.l⁻¹ or g.l⁻¹.

5.1 WATER ANALYSIS AND COMPARISON

This section deals with the analysis of the unfiltered water. The major elements were defined as elements with a concentration above 1 ppm. No significant differences were noticed when comparing major element concentrations. Changes in the concentration of minor elements (<1ppm) were noted and were caused mainly by storage problems.

5.1.1 MAJOR ELEMENT ANALYSIS

No significant differences were noticed when comparing the concentrations of major elements in the water samples (Table 3) with the exception of total inorganic carbon (TIC) changes caused by air contamination. These data were obtained by BGS using ICP, selective electrodes and ion chromatography [ROS88], CEA using ICP and ion chromatography [MOU88], JRC also using ICP and ion chromatography [BID88], PSI using AAS, selective electrodes and ion chromatography [DEG88a] and UNOS using neutron activation and ICP. CEA used various container materials for sampling/storage and measured no significant differences in the major element concentrations due to the container material (teflon, polyethylene, polypropylene). No increase in Si, Na or Ca was noticed in the water contained in glass bottles. The total inorganic carbon was, of course, affected by CO₂ contamination. AECL analyses of the ultrafiltrates are also included in Table 3 for comparison with the groundwater samples.

Table 3: Major element analysis in groundwater (ppm).

Element	BGS	CEA#	JRC	PSI	UNOS	AECL*
Na	16.2	14.7	15.9	16.0	15.8	-
Ca	6.1	5.3	5.4	5.7	4.8	2.3
Si	5.5	5.6	5.6	5.6	-	5.0
F	6.1	5.3	6.6	6.0	-	-
Cl	1.5	8.4	4.1	5.0	-	-
SO ₄ ²⁻ as S	2.2-2.1	1.8	1.6	1.9	-	-
TIC	7.3**	-	≈4	3.4	-	1.95

* ultrafiltrate analysis.

** due to CO₂ contamination.

polypropylene container.

5.1.2 MINOR ELEMENT ANALYSIS

Minor element concentrations were measured by BGS using ICP [ROS88], by CEA using ICP, LFS and a TOC unit [MOU88], by JRC using ICP [BID88], by PSI using AAS, ICPMS and a TOC unit [DEG88], by UKNP using alpha spectroscopy [LON88] and by UNOS using ICP and NA [KRE89]. The results are reported in Table 4. pH and Eh are also given. There is an order of magnitude agreement, but some differences can be observed. These are mainly due to storage problems while, in some cases, the analytical techniques were close to detection limits.

CEA observed an influence of the vessel type on Al and Fe concentrations (teflon: 70 and 70, polyethylene: 10 and <10, polypropylene 10 and <10 ppb respectively). While the pH may occasionally drop to about 8 due to CO₂ contamination, and the in-situ pe of 0 (PSI) may rise to 6.5 (JRC) due to O₂ contamination, the minor element concentrations were reasonably similar (PSI) when the water was stored in glass or teflon bottles. Some contamination from the container must be mentioned, such as Zn for the teflon containers. Uranium concentrations measured (PSI) by ICPMS (rapid scan) and by colorimetric techniques were below the detection limit of about 0.05 ppb; subsequent analysis by quantitative ICPMS gave a uranium concentration of 0.03(±0.03) ppb. Alpha spectrometric (ANS) counting gave 0.15 ppb and this concentration remained fairly constant over the period from November'87 to May'88. Discrepancies are due to the fact that these analyses are close to the detection limits.

UKNP and AECL analyses of their ultrafiltrates are reported for comparison purposes in Table 4.

Table 4: Minor element analysis in groundwater (ppb).

Element	BGSa	CEAa-d	JRCa	PSIab	UNOSa	AECL*	UKNP*
Li	72	-	71	85	-	-	-
Be	-	-	-	0.5	-	-	-
B	64	-	141	93a	90	-	-
Mg	<140	-	9.7	49-10	60	5.6	-
Al	<60	70-10	5.3	47-15	30	<200	-
K	<1000	140-80	-	140-40	-	-	-
Sc	-	-	-	14	21	-	-
Ti	-	-	-	3	-	-	-
V	<20	-	-	≤0.1	-	-	-
Cr	<120	-	-	0.4-0.2	1.1	-	-
Mn	<4	<10	<2	2-0.3	-	-	-
Fe	<20	70-<10	<2	35	29	<20	-
Co	<35	-	-	0.05	0.09	-	-
Ni	<85	-	-	≤1	-	-	-
Cu	<15	-	-	0.5-0.2	-	-	-
Zn	<30	-	-	27b-0.5a	1.0	-	-
Ga	-	-	-	0.5	-	-	-
Ge	-	-	-	0.5	-	-	-
As	-	-	-	0.3	-	-	-
Se	-	-	-	8-5	-	-	-
Br	<100	-	-	30	52	-	-
Rb	-	-	-	1.4	-	-	-
Sr	179	160	150	200-170	170	73	-
Y	-	-	-	≤0.02	-	-	-
Zr	<45	-	-	0.1	-	-	-
Nb	-	-	-	0.05	-	-	-
Mo	<50	-	-	20	-	-	-
Ru	-	-	-	0.1	-	-	-
Pd	-	-	-	0.1	-	-	-
Ag	-	-	-	≤0.07	-	-	-
Cd	<5	-	-	<0.1	-	-	-
Sn	-	-	-	0.7	-	-	-
Sb	-	-	-	<0.2	0.4	-	-
Te	-	-	-	≤0.2	-	-	-
I	-	-	-	0.1	-	-	-
Cs	-	-	-	1-0.5	0.72	-	-
Ba	<1	-	3	0.5	-	-	-
W	-	-	-	70	-	-	-
Hg	-	-	-	3-<0.1	-	-	-
Tl	-	-	-	≤0.1	-	-	-
Pb	<100	-	-	≤0.6	-	-	-
Th	-	-	-	<0.05	-	-	0.024
U	-	0.05b-0.01c	-	0.15-0.03	-	0.076	0.035
pH	7.9	-	9.54	9.56	-	-	9.5-8
pe	-	-	6.5	0.0	-	-	-
TOC	-	900	-	500-200	-	570	-

* on the basis of analysis of the ultrafiltrate.

a glass container.

b teflon container

c polyethylene container.

d polypropylene container.

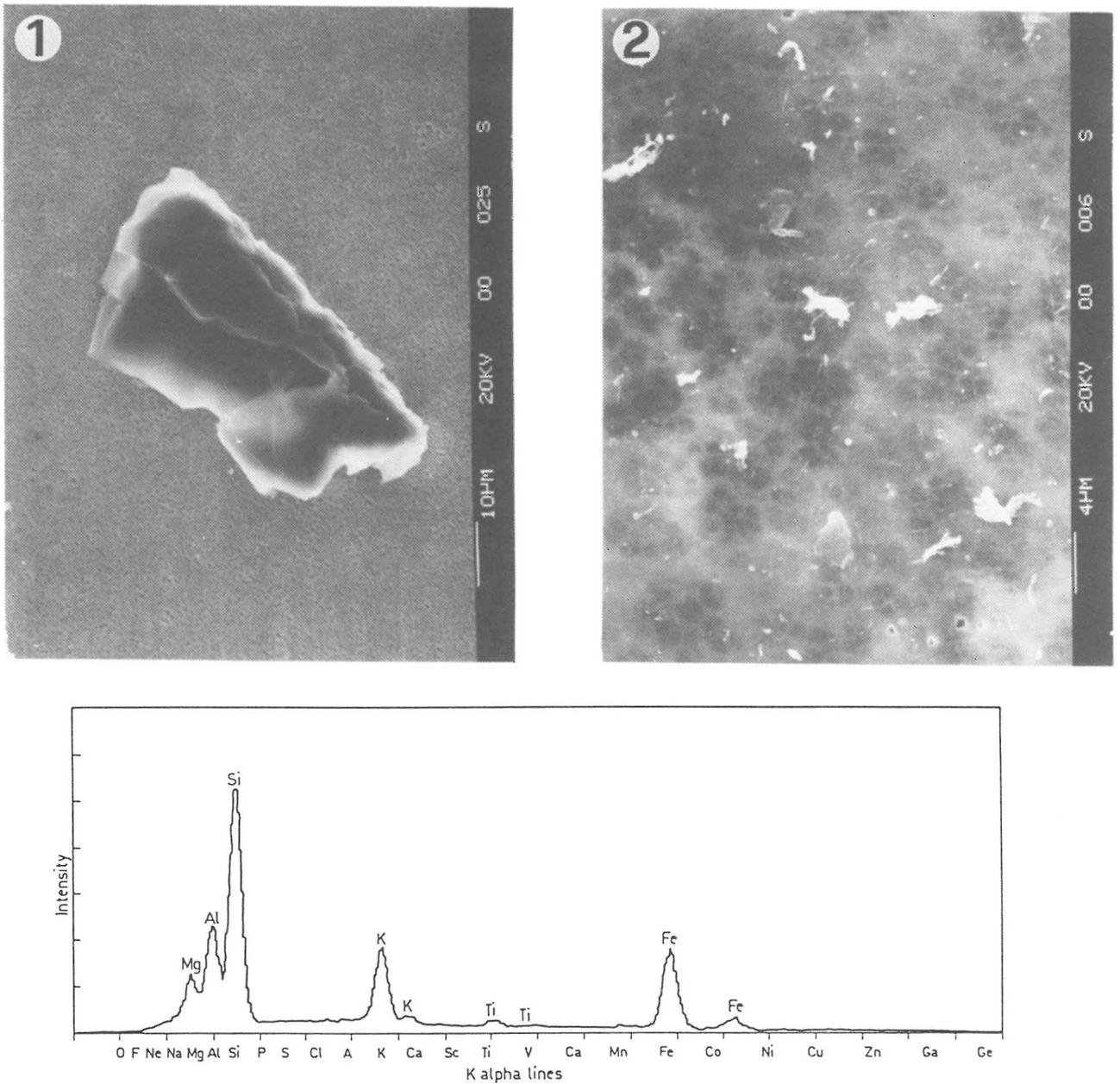


Figure 7: Typical BGS SEM micrographs and EDS analysis of CEA colloid samples.

Conditions: micrograph 1: biotite particle on 220 nm CEA4 filter
 micrograph 2: colloids on 15 nm CEA2 filter, typical population
 EDS spectrum of the particle on micrograph 1.

5.2 ANALYSIS OF COLLOID SAMPLES PREPARED ON SITE

In this section, colloid samples prepared on site by cross-flow filtration (CEA, PSI) for SEM investigation and by tangential filtration concentration (AECL) for gravimetry tests are considered.

5.2.1 CROSS-FLOW FILTRATION SAMPLES

These investigations involve membranes loaded on site with the colloids. Analyses were performed by BGS, CEA, PSI, UKNP and VTT. All particle counting is translated into particle/colloid concentration and the calculation is reported either by size class $[\varnothing, \varnothing+d\varnothing]$:

$$\frac{\delta[\text{coll}]}{\delta\varnothing} = \frac{1000}{V} \cdot \frac{S_{(\text{act})}}{\sum_{i=1}^n s_{(i)}} \cdot \sum_{i=1}^n N_{(i, \varnothing)} \quad [5.1]^*$$

or as a global colloid population for sizes ranging from a minimum diameter $\varnothing_{(m)}$ to a maximum $\varnothing_{(M)}$:

$$[\text{coll}] = \frac{1000}{V} \cdot \frac{S_{(\text{act})}}{\sum_{i=1}^n s_{(i)}} \cdot \sum_{i=1}^n \int_{\varnothing_{(m)}}^{\varnothing_{(M)}} N_{(i, \varnothing)} \cdot d\varnothing \quad [5.2]$$

with n images (video or micrographs), $N_{(i, \varnothing)} \cdot d\varnothing$ particles counted between \varnothing and $\varnothing+d\varnothing$ on the image i , $s_{(i)}$ the microscopic area of the image i and $S_{(\text{act})}$ the active area of the membrane. In these formulae, the colloid concentration $[\text{coll}]$ is expressed in pt.l^{-1} while the volume is expressed in ml. [5.1] and [5.2] are valid under the following assumptions: the recovery of colloids is quantitative on the membrane and the preparation treatment does not alter the colloidal phase on the membrane prior to GRAV or SEM investigation.

BGS [ROS88] analysed the CEA and PSI membranes prepared on site, after coating with carbon, by SEM (Cambridge Instruments Stereoscan 250). Particles collected and identified by EDS (Link Systems 860) commonly included silica, biotite (Figure 7), muscovite, quartz, Fe hydroxide and organic material. A series of eight to ten representative photographs were taken at equal intervals along a radius at 3,000 and 6,000 magnification. This yielded a field size or count area of about 1000 and 250 μm^2 and a lower particle size limit $\varnothing_{(m)}$ in the order of 200 and 100 nm respectively (the size resolution is in the order of 50 nm).

Table 5: BGS colloid concentrations obtained by SEM counting of the CEA and PSI samples prepared on site.

Sample	volume/ml	pore-size/nm	magnification	$[\text{coll}]/\text{pt.l}^{-1}$	$\varnothing_{(m)} - \varnothing_{(M)}/\text{nm}$
CEA1	20	3	3,000	$86 \pm 27 \cdot 10^8$	200-1,000
CEA1	20	3	6,000	$170 \pm 48 \cdot 10^8$	100-1,000
CEA2	20	15	3,000	$19 \pm 3 \cdot 10^8$	200-1,000
CEA3	20	15	3,000	$25 \pm 3 \cdot 10^8$	200-1,000
CEA4	20	220	3,000	$22 \pm 6 \cdot 10^8$	200-1,000
PSI1	76	3	3,000	$8 \pm 3 \cdot 10^8$	200-1,000
PSI2	44	3	3,000	$9 \pm 1 \cdot 10^8$	200-1,000
PSI3	46	3	5,000	$12 \pm 2 \cdot 10^8$	100-1,000
PSI4	26	3	5,000	$14 \pm 2 \cdot 10^8$	100-1,000
PSI5	150	3	5,000	$4 \pm 1 \cdot 10^8$	100-1,000

* In this report the absolute value is used in agreement with literature [BUF88].

CEA [MOU88] carried out SEM counting of their membranes and of PSI membranes. Preparation of membranes (cutting, pasting) was carried out under controlled conditions. The laboratory used a Balzers apparatus to coat the membranes with gold. CEA analysed the membrane with a Jeol SEM under a magnification of 5,000-40,000. A field size ranging from 500 to 68,000 μm^2 (for high porosity) was observed according to membrane type. EDX analyses were also performed with a Tracor system. While the counting on the UF membrane is not affected by the microscopic structure of the membrane (CEA1-3 samples), colloid observation on the MF membranes (CEA4-6) is more difficult due to their porous structure. For the CEA1-3 membranes, CEA observed the presence of some bacteria ($>1\mu\text{m}$), dispersed and aggregated particles, some rock fragments and a lot of spherical particles; on the PSI membranes, dispersed and aggregated particles, rock fragments, very small spherical particles and also some particles in the blank zone were observed. For a total colloid concentration of $4.2 \cdot 10^9 \text{ pt.l}^{-1}$ ($\bar{\varnothing}_{(m)} > 70\text{nm}$), the size distribution of 14% $> 100\text{nm}$, 4% $> 220\text{nm}$, 0.6% $> 450\text{nm}$ can be derived. The EDS spectra reveal the presence of Si from "fragment" particles and also spherical colloids. The presence of Al, Na and Ca is also detected for some particles. Most of the particles do not exhibit a spectrum different from the blank. Figure 8 shows typical micrographs together with the corresponding image analysis of colloid areas, prior to size distribution analysis.

Table 6: CEA colloid concentrations obtained by SEM counting of the CEA and PSI samples prepared on site.

Sample	V/ml	pore-size/nm	magnification	[coll]/pt.l ⁻¹	$\bar{\varnothing}_{(m)} - \bar{\varnothing}_{(M)}$ /nm
CEA1*	20	3	40,000	$4.5 \cdot 10^9$	70-1,000
CEA2	20	15	20,000	$3.8 \cdot 10^9$	70-1,000
CEA3	20	15	40,000	$4.4 \cdot 10^9$	70-1,000
CEA4	20	220	5,000	$1.8 \cdot 10^8$	220-1,000
CEA5	20	100	5,000	$6.0 \cdot 10^8$	100-1,000
CEA6	20	450	5,000	$2.6 \cdot 10^7$	450-2,000
PSI1*	76	3	40,000	$1.3 \cdot 10^8$	70-1,000
PSI3*	46	3	40,000	$6.5 \cdot 10^8$	70-1,000

* counting by image analysis.

PSI has been using the combination of PDUF and SEM for the last three years [DEG87c,DEG89]. The analyses were carried out with a Cambridge Instrument after pasting and coating the sample on an Al sample carrier. Coats of Au or Au/Pd are in the order of 10 nm and, at the moment, particles below 40 nm cannot be resolved with any certainty. All the samples (PSI, CEA) were analysed with a primary magnification of 10,000. Each negative of the micrograph was developed with 3 different contrast grades and the final magnification was 22,000. These A4 positive micrographs were studied on a quantimeter (Cambridge Instruments Quantimet 920) including a video camera, an image analyser and a recorder. A size distribution is printed out for each micrograph or each series. A contrast grade study was carried out before any routine quantification. Here, the colloid size is the equivalent diameter of the circle which has the area of the single colloid (or of the aggregate when two (or more) colloids contact together). The Quantimet, however, allows the counting of the aggregate as a sum of separated colloids with an "erosion" (image deconvolution) program. This separate quantification is limited to overlaps of about 50%. The 5 PSI membranes were observed from $\bar{\varnothing}_{(m)} = 40 \text{ nm}$ with a $d\bar{\varnothing}$ of 40 nm. For this exercise, the study was carried out as a function of the volume (V) of water. The filtration geometry deals with the ratio between this volume and the active surface $S_{(act)}$ and the height of filtered water $H = V/S_{(act)}$ is the key parameter. The specific size distributions are reported in Figure 9. The size distributions are comparable for the classes of large colloids, while the aggregation yielded by increasing V (PSI-1 and PSI-5) depresses the specific size distribution for the classes of small colloids. This behaviour is studied quantitatively in section 6 (Figure 21) where both integral and differential specific size distribution are compared.

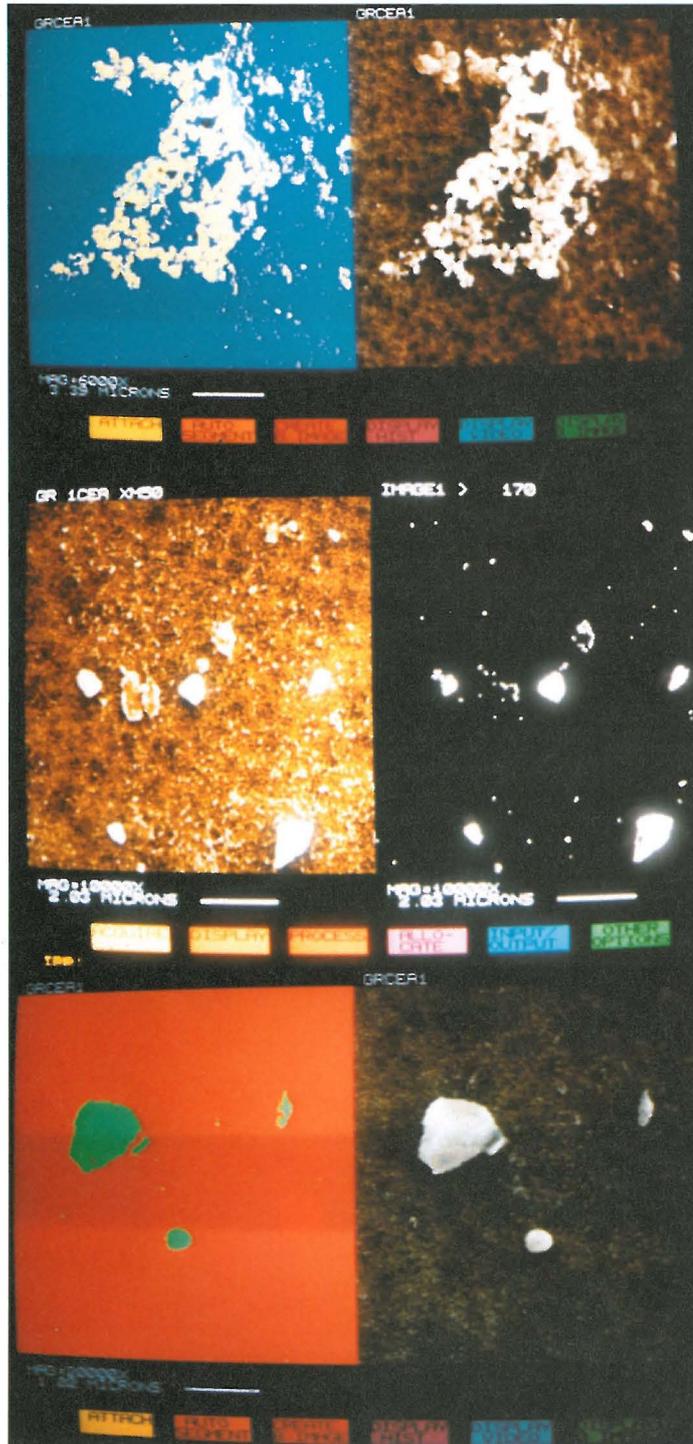


Figure 8 : Some typical CEA micrographs of CEA1 and their image analysis.

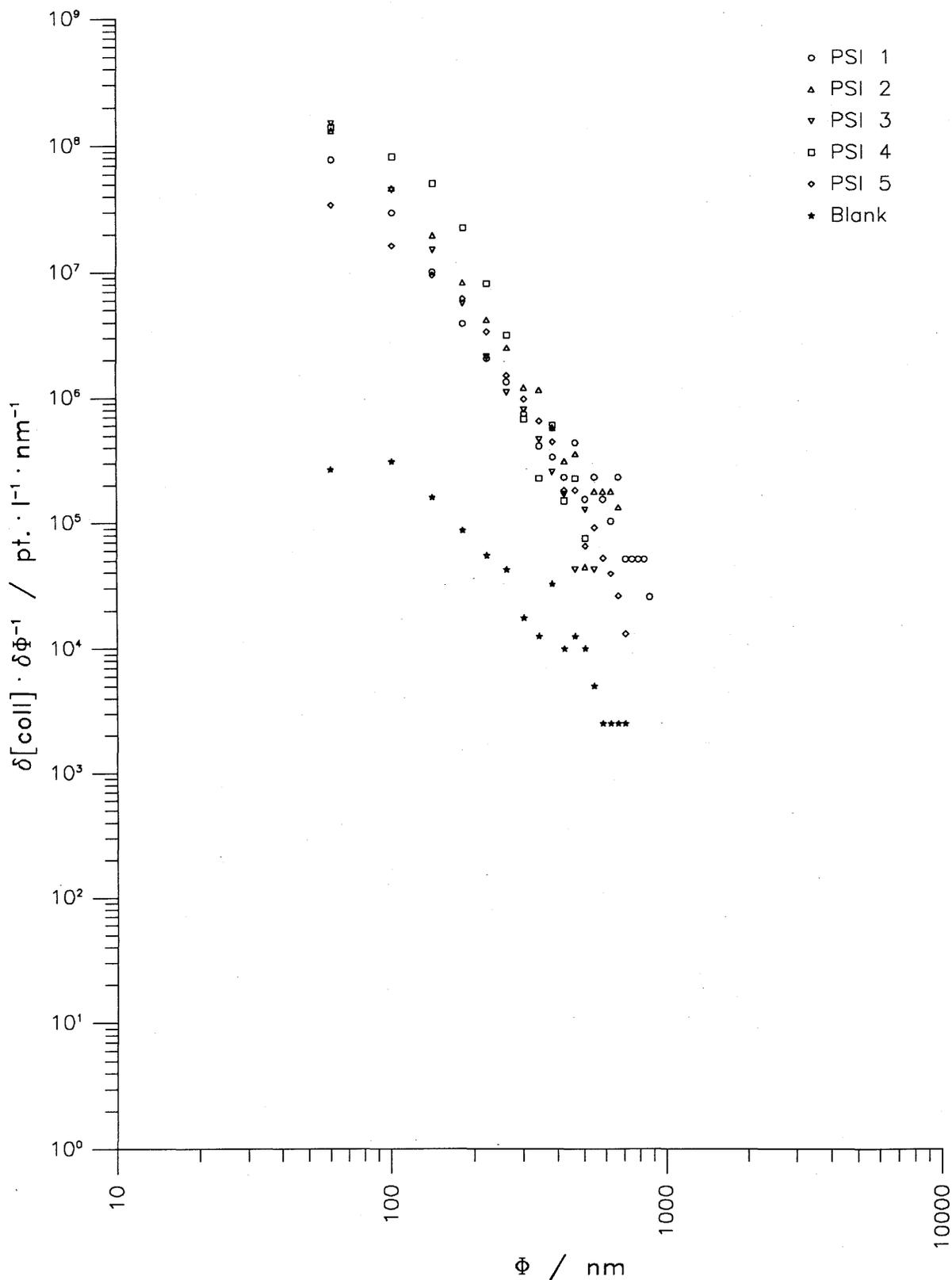


Figure 9: PSI SEM specific size distribution of PSI 1-5 samples.
 The sample volumes were 76 ml (PSI1), 44 ml (PSI2), 46 ml (PSI3),
 26 ml (PSI4) and 150 ml (PSI5).

PSI also performed a sensitivity study on the PSI4 membrane and Figure 10 shows both profiles for the same $\varnothing_{(min)}$ (i.e 40 nm) but also for $d\varnothing$ of 10 and 40 nm together with an erosion study. The values derived from $d\varnothing = 10$ nm are selected as the PSI recommended results.

PSI also analysed the CEA colloid sample on the membrane prepared on site and Table 7 reports the colloid and particle concentrations counted for PSI and CEA samples. CEA colloid sample specific size distributions are presented in section 6 together with the PSI results obtained with the CEA1-5 samples.

Table 7: PSI colloid concentrations obtained by SEM counting of the CEA and PSI samples prepared on site.

Sample	V/ml	pore-size/nm	[coll]/pt.l ⁻¹	$\varnothing_{(m)}/nm$	[part]/pt.l ⁻¹	$\varnothing_{(m)}/nm$
PSI1	76	3	5.1 10 ⁹	40	7.2 10 ⁷	450
PSI2	44	3	8.7 10 ⁹	40	4.7 10 ⁷	450
PSI3	46	3	8.9 10 ⁹	40	1.7 10 ⁷	450
PSI4	26	3	1.2 10 ¹⁰	40	1.6 10 ⁷	450
PSI5	150	3	3.0 10 ⁹	40	1.9 10 ⁷	450
CEA1	20	3	6.6 10 ¹⁰	40	5.8 10 ⁷	450
CEA2	20	15	4.8 10 ¹⁰	40	5.7 10 ⁷	450
CEA3	20	15	3.7 10 ¹⁰	40	1.9 10 ⁸	450

UKNP [LON88] analysed CEA and PSI membranes with an Hitachi S520 at magnifications of 5,000 and 10,000. Micrographs were taken along the two intersecting perpendicular chords in order to ascertain the variation of colloid population across the sample. Colloids and particles were counted visually and converted to colloid concentrations per litre (Table 8). Because of the difference in the counting from one micrograph to another, the standard deviation is fairly large. UKNP estimate the detection limit to be 80 nm and 50 nm for the magnifications of 5,000 and 10,000 respectively. The blank is estimated on an XM50 Amicon membrane washed with Analar water to remove the protective glycerol coating. With a magnification of 5,000 and counting from 0.3 to 1.0 μm , a blank concentration of 10⁵ pt.l⁻¹ is measured for a volume of 20 ml of Analar water.

Table 8: UKNP colloid concentrations obtained by SEM counting of the CEA and PSI samples prepared on site.

Sample	V/ml	Pore-size/nm	Magnification	[coll]/pt.l ⁻¹	$\varnothing_{(m)} - \varnothing_{(M)}/nm$
PSI2	44	3	5,000	3.0 ± 0.2 10 ⁸	100-1,000
PSI4	26	3	5,000	1.9 ± 0.1 10 ⁹	100- 200
PSI4	26	3	10,000	6.9 ± 0.4 10 ⁹	50-1,000
CEA1	20	3	10,000	1.9 ± 0.1 10 ¹⁰	50- 300
CEA4	20	220	5,000	10 ⁷ - 10 ⁸	300-1,000

VTT [VUO87] counted the colloids on membrane PSI5 visually without using an image analysis system. The drying treatment was carried out at 50 °C. VTT results [VUO88] are presented in section 6 (Figure 20) and compared with PSI counting. Comparing the EDS spectra of both active and inactive areas of the PSI5 membrane, VTT detected Si, Al, Mg, Fe, K and Na as the major elements of the colloidal phase.

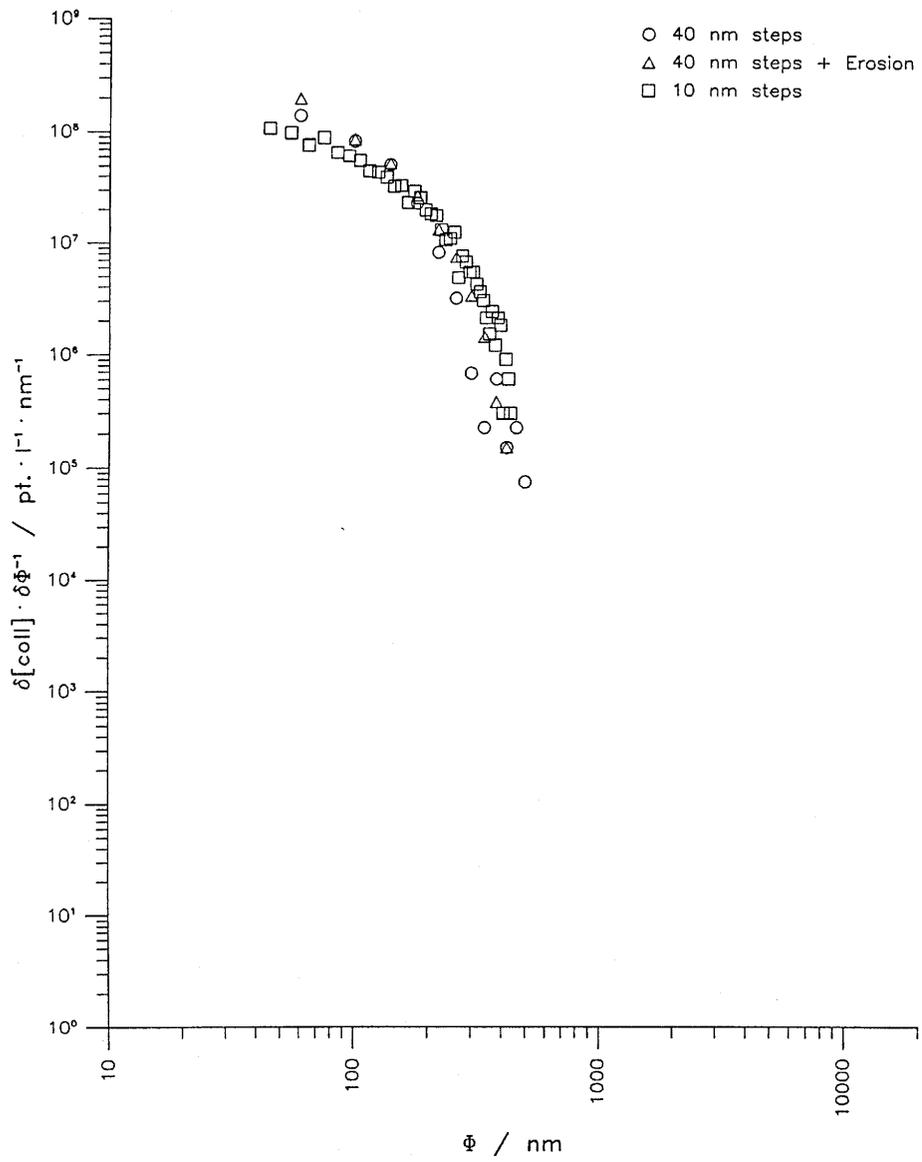


Figure 10: PSI sensitivity and erosion study on the PSI4 sample.

5.2.2 TANGENTIAL FLOW FILTRATION CONCENTRATES

AECL [VIL88a] produced a second concentrate sample (AECL2) on site, directly after preparing the concentrate for the CoCo Club members. Immediately after the concentrate with particles greater than 1 nm had been produced with the Pellicon system, this concentrate was filtered with the Minitan tangential flow filtration system equipped with 240 cm² of Durapore membrane with a 450 nm cut-off. This microfiltration produced a filtrate containing colloids between 1 and 450 nm and a concentrate which was enriched by a factor of 2 (vs the former concentrate) with particles larger than 450 nm. AECL then applied its gravimetric scheme (GRAV) with the sequential separation of the particles through a series of Nuclepore membranes with cut-off sizes of 10,000, 5,000, 400, 100, 50 and 10 nm.

Shortly after colloid sampling, 40 ml of the concentrate, enriched in particles larger than 450 nm, was filtered in series through the 25 mm polycarbonate filters with cut-off sizes from 10,000 to 400 nm. The solutions were forced through the filters using 50 ml syringes. The concentrate with colloids smaller than 450 nm was filtered in series through the 100 nm and smaller pore-size membranes using a syringe weighted with 6 kg of lead bricks. The filtration procedure was carried out without the protection of a nitrogen atmosphere and lasted approximately 90 minutes. The weights of the Nuclepore membranes before and after filtration were measured in duplicate at AECL using an electronic Sartorius balance with a sensitivity of 0.01 mg. Table 9 reports the specific size distribution of the colloid with in-situ separation. The assumptions made are that there are no losses and no artefact production during the fractionation (TDUF, MF, UF). In addition, samples for XRD were prepared at Grimsel by filtering 80 ml of colloid concentrate through a 25 mm silver membrane with a cut-off of 200 nm. In order to prepare a blank, 80 ml of Grimsel water were passed through another silver membrane. The XRD powder pattern was consistent with either illite or muscovite. Calcite was not detected.

Table 9: AECL gravimetry results with the colloid samples prepared on site.

Size/nm	[coll]/mg.l ⁻¹	Ø _(a) /nm	δ[coll].δØ ⁻¹ /ng.l ⁻¹ .nm ⁻¹
10 - 50	0.038	30	950
50 - 100	0.051	75	1,020
100 - 400	0.045	250	150
400 - 5,000	0.040	2,700	8.7
5,000 - 10,000	0.020	7,500	4.0
>10,000	0.048		

Total	0.242		

Conditions: the particle concentration is adjusted to the original groundwater. The average of δ[coll].δØ⁻¹ is 9.7 ng.l⁻¹.nm⁻¹ and the average size for the range 10 - 25,000 nm is 2,500 nm. The difference in the results of the duplicate determination was typically 10% and in no case more than 20%.

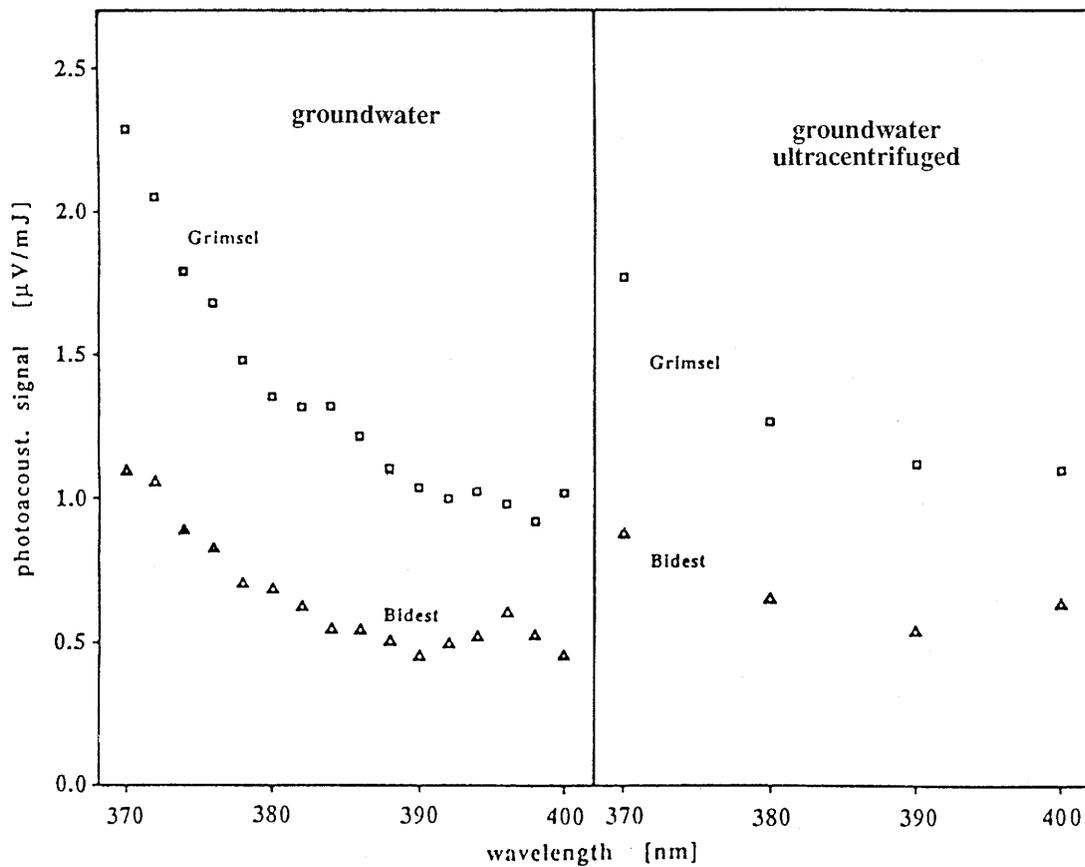


Figure 11: TUM laser induced-photoacoustic spectra of the filtered (0.45 µm) groundwater and of the ultracentrifuged sample. (Bidest = double distilled water).

5.3 COLLOID ANALYSIS OF FLUID SAMPLES IN THE LABORATORY

Since the fluid samples (unfiltered water and concentrate) may present some stability problems, investigation of the fluid sample may be carried out in the laboratory after storage under reasonable conditions ($T = 285\text{K}$, $P_{(\text{O}_2)}$ and $P_{(\text{CO}_2)} < 10^{-6}$ Atm). The sample may be contaminated by CO_2 (or O_2) and, as reported by UKNP [LON88], the pH of concentrate samples may drop from 9.5 to about 8. Here again, plastic containers (or leaky stoppers) should be avoided because of their permeability for CO_2 and O_2 .

5.3.1 CROSS-FLOW FILTRATION SAMPLES

SEM analyses of membranes loaded with colloids ultrafiltered in the laboratory were performed by PSI, CEA, TUM and UKNP.

CEA analysed colloid samples on membranes after separation in the laboratory. These samples were produced from the AECL concentrate and from unfiltered water. The membranes used were the Amicon XM300 with a pore diameter of 15 nm. The ultrafiltration cell is an Amicon 8010 ($V=10\text{ml}$, stirring). The population of particles larger than 70 nm was $4.0 \cdot 10^9$ and $9.8 \cdot 10^8 \text{ pt.l}^{-1}$ for the unfiltered water and for the AECL sample corrected with its enrichment factor respectively.

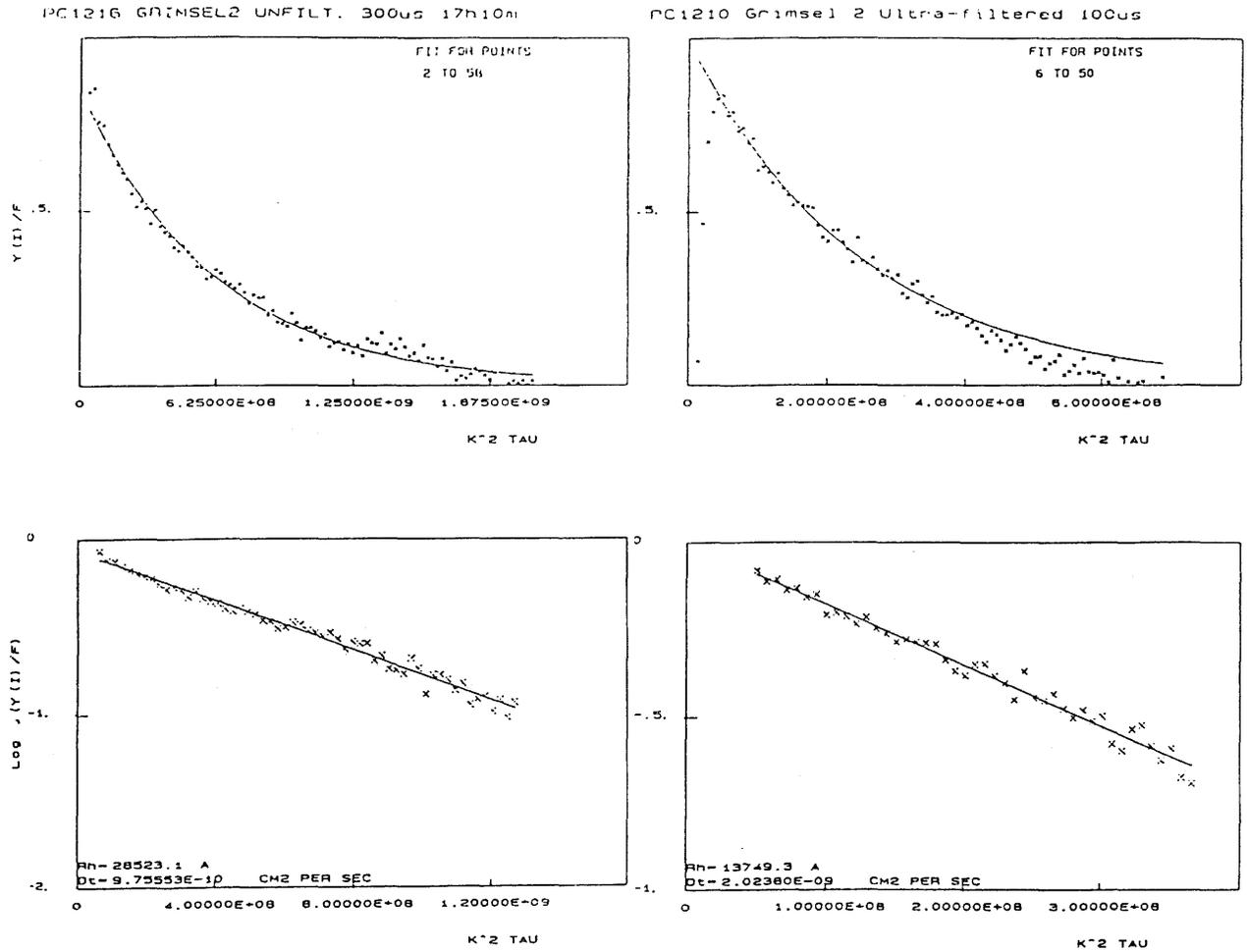
PSI also performed tests combining UF and SEM on water samples and concentrates from AECL (48X) and UKNP (38X). A variety of membranes were used in this series of tests: PSI1' and 2' - Amicon XM50 (polyacrylamide); PSI1" to 3" - XM300 (polyacrylamide); PSI4" - YM01 (polysaccharide); PSI5" - PM10 (polysulphone). The UF methodology is as described earlier and the SEM counting was carried out as described in section 5.2.1. The results are reported in Table 10.

Table 10: PSI colloid concentration by ultrafiltration in the laboratory.

Sample	V/ml	pore-size/nm	[coll]/pt.l ⁻¹	$\varnothing_{(m)}$ /nm	[part]/pt.l ⁻¹	$\varnothing_{(m)}$ /nm
Concentrate						
PSI1' UKNP	2	3	$5.8 \cdot 10^9$ *	40	$1.6 \cdot 10^8$ *	450
(76)		3	$1.5 \cdot 10^8$	40	$4.2 \cdot 10^6$	450
PSI2' AECL	2	3	$3.9 \cdot 10^{10}$ *	40	$1.0 \cdot 10^9$ *	450
(96)		3	$8.1 \cdot 10^8$	40	$2.2 \cdot 10^7$	450
Groundwater						
PSI1"	45	15	$8.4 \cdot 10^9$	40	$1.2 \cdot 10^7$	450
PSI2"	25	15	$1.1 \cdot 10^{10}$	40	$1.3 \cdot 10^7$	450
PSI3"	10	15	-		-	
PSI4"	5	1	$3.8 \cdot 10^8$	40	-	450
PSI5"	20	1.5	$7.0 \cdot 10^8$	40	$1.6 \cdot 10^7$	450

* concentration in the concentrate; the corrected value for the original sample is given in the following line.

TUM [KIM88] used SEM to analyse the colloid sample prepared on membranes by PSI in the laboratory (Figure 3). A quantitative size distribution is plotted in section 6 (Figure 24) for the filter obtained with 2 ml of the AECL concentrate (20.9X). The colloid concentrations determined in two SEM countings were 0.6 and $1.5 \cdot 10^9 \text{ pt.l}^{-1}$.



PCS autocorrelation function
Grimsel water (26.11.87).

PCS autocorrelation function
Grimsel ultrafiltrate XM50.

Figure 12: Typical UKC dynamic light scattering spectra of the Grimsel groundwater and its ultrafiltrate.

VTT and TUM also analysed the PSI4"-5" samples by SEM and confirmed the low colloid concentration ($\approx 10^8$ pt.l⁻¹). This could be due to the fact that the colloid does not adhere to these membranes after separation.

AECL [VIL88a] determined the size distribution in the laboratory by filtering groundwater samples shipped to AECL and using the gravimetric approach described in section 5.2.2. The separation work performed in May'88 was carried out in a glove-box filled with nitrogen. The specific size distribution is reported in Table 11 together with data for a blank of filtered ultrapure water. Two points should be noted: firstly, the measured colloid concentrations in the blank are surprisingly high; secondly, the differences between duplicate determinations of the blank colloid concentrations were also high: in fact some determinations gave negative values.

Table 11: AECL gravimetry results with the groundwater shipped to the laboratory and with a blank.

Particle concentration adjusted to the original water.

$\emptyset_{(m)} - \emptyset_{(M)} / \text{nm}$	$[\text{coll}] / \text{mg.l}^{-1}$	$[\text{coll}]^* / \text{mg.l}^{-1}$	$\emptyset_{(a)} / \text{nm}$	$\delta[\text{coll}] \cdot \delta\emptyset^{-1} / \text{ng.l}^{-1} \cdot \text{nm}^{-1}$
10- 50	0.262	0.022	30	6,550
50- 100	0.225	0.000	75	4,500
100- 400	0.300	0.028	250	1,000
400- 5,000	0.249	0.081	2,700	54.1
5,000-10,000	0.062	0.000	7,500	12.4
>10,000	0.062	0.022		
-----	-----	-----	-----	-----
Total	1.160	0.131		

*Blank: with ultrapure water.

5.3.2 FLUID SAMPLES

Colloids from the fluid samples were studied using photon interaction techniques, electron microscopy and chemical or isotopic analysis of the separated phases.

5.3.2.1 Tests with photon interaction techniques

Laser photoacoustic measurements and static and dynamic light scattering tests were carried out by TUM and UKC respectively prior to the benchmark exercise. Since the colloid concentration was found to be constant at the kalotte, these LPAS and SLS/DLS results are reported for the sake of comparison.

TUM [KLE86] performed the LPAS investigations with Grimsel groundwater samples which were delivered in glass bottles in October'86 together with other groundwater samples and double-distilled water as a "blank". Prior to measurement, water samples were filtered (450 nm) and 4 ml were injected into a 2 cm quartz cuvette. Grimsel water exhibits light attenuation in the visible and the UV region compared with the blank (Figure 11). In the UV-region below 390 nm, all waters show an increase in the photoacoustic signal with decreasing wavelength. The slope at 370 nm should depend on scattering, and should thus give an approximate estimation of the concentration of colloids in the solution. Differences in the photoacoustic signal in other regions (465-600 nm) are caused by the absorption of minor and trace components. The measurements were repeated after separating the Grimsel colloids by ultracentrifugation (600,000 g/24h). After centrifugation, the photoacoustic signal is reduced, particularly at the blue side (about 30% at 370 nm). To a lesser extent the spectra in the visible range are also influenced by centrifugation, indicating that some of

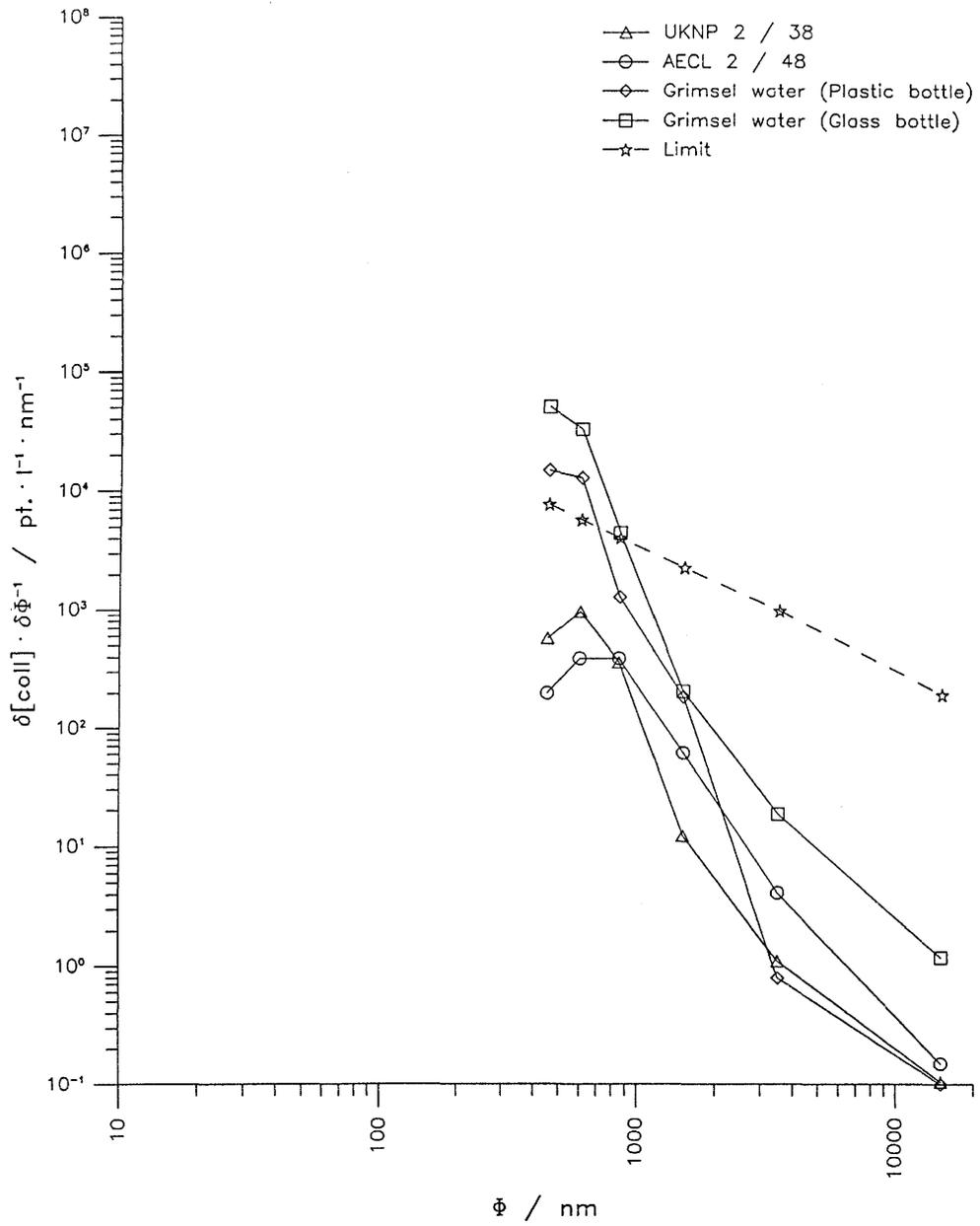


Figure 13: PSI particle counting tests on fluid samples.

the absorbing species are also separated out. However, the photoacoustic signal of double distilled water increased by about 30% compared to the Grimsel sample. As this increase is found after centrifugation in plastic tubes, it was assumed that this effect was due to contamination of the waters by organic substances during the sample handling.

UKC [NIC88] investigated the Grimsel groundwater samples using static and dynamic light scattering (SLS and DLS). The samples were taken and prepared by PSI (unfiltered groundwater, concentrate and ultrafiltrate) in October and November'87 and shipped express to Harwell. Initial measurements were made with a 40 mW red He-Ne laser. This laser was soon replaced by a blue He-Cd laser of comparable power output but significantly greater scattering intensity due to the shorter wavelength of light. The scattered light was analysed with a Malvern unit . The time-averaged intensity (SLS) of scattered laser light (90°) for the different groundwater samples is shown in Table 12 . The measured count rates are all above the background level obtained with filtered (0.02µm) distilled water. The count rates tend to fluctuate (when measured over one second) due to larger particles drifting through the laser beam. Exposing one of the Grimsel samples to air (for 2 weeks) had no effect on the average scattering intensity. The count rate from the Grimsel concentrate (30X) was high but the intensity was not 30 times greater. Finally UKC estimated the size of the colloids by counting the filtrates obtained by microfiltration. The Grimsel groundwater was filtered through 1.0 and 0.1 µm Nuclepore polycarbonate membrane filters. The 1.0 µm filter did not significantly decrease the counting rate and a 0.1 µm filtration was necessary to reduce scattering to background level.

Table 12: UKC results from static light scattering tests.
Scattered light intensities from the groundwater samples.

Water sample -----	Count rate (cps) -----
Filtered distilled water	900
Grimsel (27.10.87/glass bottle)	2,000-4,000
Grimsel (27.10.87/glass) exposed to air	2,500-3,500
Grimsel (27.10.87/plastic bottle)	1,600-1,800
Grimsel (26.11.87/plastic bottle)	900-1,500
Grimsel ultrafiltrate XM50 (25.11.87)	2,200
Grimsel 30X concentrate (30.11.87)	1,600-5,000

UKC also performed DLS measurements, and some representative groundwater sample spectra are shown in Figure 12. The best exponential decays were obtained using sample times in the order of 100 µs which correspond to translational diffusion coefficients of 10⁻⁹ cm².s⁻¹ and hydrodynamic radii (assuming spherical particles) of 2 to 3 µm. The Grimsel concentrate was filtered (1.0 µm Nuclepore) to remove larger particles. However, DLS measurements of the filtrate did not indicate the presence of submicron particles only. A background DLS spectrum (3 nm filtered groundwater) is shown in Figure 12.

PSI particle counting tests [DEG88a] were performed by transmission measurements with an Hiac/Royco counter which measures the number of particles for 6 size classes (0.4-0.5, 0.5-0.7, 0.7-1.0, 1.0-2.0, 2.0-5.0, 5.0-25.0 µm). Counting was carried out in a flowing system (200 ml.min⁻¹) and was finally integrated for the given volume of fluid sample (200ml). Calibration was performed using monosized spheres which are defined by methods traceable to NBS and using "AC" Fine Test Dust (International Standards Organization, American National Standards Institute). Measurements were carried out at Skan AG in Basel. The upper detection limit was reported as a maximum specific size distribution for the experimental counting geometry. The upper detection limit shown on the Figure 13 was derived for the experimental counting geometry using information supplied by the equipment manufacturer. Above this maximum, the counting is not proportional to the particle concentration because the probability of one particle obscuring another increases. Results for unfiltered water stored in plastic and glass bottles are presented together with both concentrate

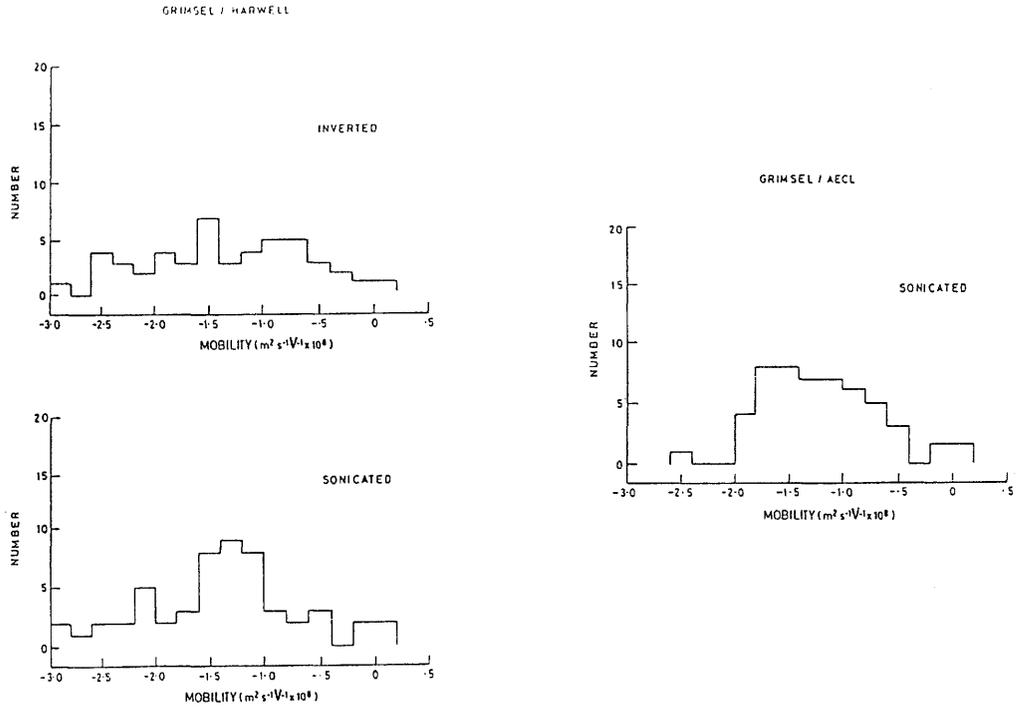


Figure 14: UKNP microelectrophoretic spectra of the fluid samples.

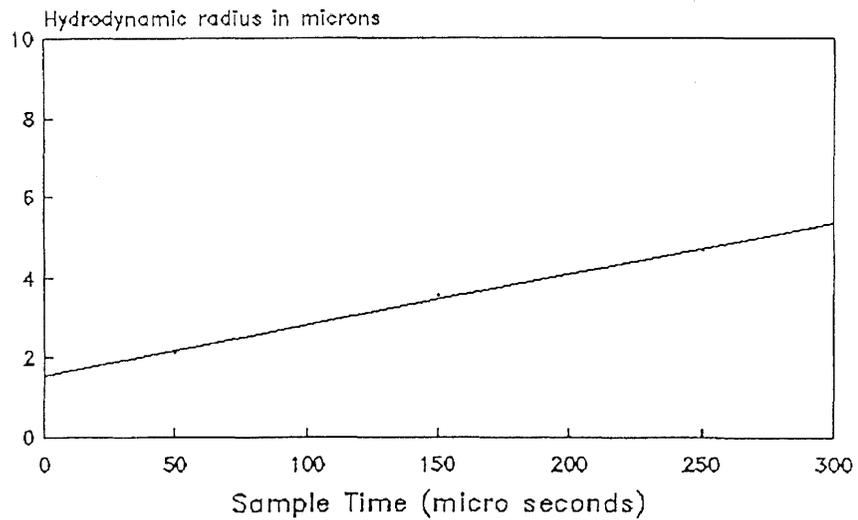


Figure 15: UKNP dynamic light scattering test, size analysis by extrapolation to zero sampling time.

samples (UKNP in glass bottle and AECL in a polyethylene bottle) in Figure 13. The reproducibility from one run to another is about 5%. Profiles from both unfiltered water samples are similar, but the colloidal sample in the glass bottle is more concentrated than the sample stored in the plastic bottle. Given the fairly high pH of the water, most of the colloid material should be negatively charged like the glass surface itself, but this is not the case for plastics such as polyethylene. Some particles may stick to the plastic while this seems to be unlikely for glass. For the concentrates, the particle concentration measured was 4-6 times smaller (after correction with the enrichment factor) than the concentration of the original water. In addition, the UKNP concentrate which should be depleted in particles (1 μm prefiltration) presents a significant concentration of large particles, suggesting, if the prefiltration is efficient, that the colloids aggregate to generate larger particles. This is confirmed by the SEM work and also by the natural behaviour of a strong Grimsel concentrate (AECL, 384 times) which settled out of solution after 1 month. The concentration in the AECL (X48) concentrate did not correspond to the specific size distribution of the water multiplied by 48. Here again the same reason can be invoked as for the UKNP concentrate. The aggregation observed is a function of the colloid concentration [NAK86,FLO53].

UKNP [LON88] performed experiments combining particle counting and microelectrophoresis. These were carried out at the Freshwater Biological Association, Ambleside. A Rank Brothers MKII apparatus was used with a flat cell of dimensions 1.095 by 9.70 mm. Particle images were displayed on a TV screen and the numbers within grids of volume $1-6 \cdot 10^{-5} \text{ cm}^3$ were counted, correcting for coincidence. The detection limit for particle counting depends upon the refractive index and is difficult to quantify, but is expected to be in the range 0.2 - 1 μm . The fluid samples were either inverted or sonically treated to disperse any loose aggregates. Results of particle counting are reported in section 6 and Figure 14 shows mobility spectra for both the unfiltered water and the AECL concentrate. The colloid concentration of about 10^9 pt.l^{-1} agrees with that determined by SEM (with the same lateral resolution). The value for the AECL concentrate is not appreciably higher than that for the unfiltered water, while that for UKNP is a factor of 5 higher, but still less than the concentration factor of 28. The mean mobilities are $-(1.4 \pm 0.7)$ and $-(1.2 \pm 0.5) \cdot 10^{-8} \text{ m}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$ for unfiltered water and the AECL colloid concentrate, with a large spread in values between -3 and $+0.25 \cdot 10^{-8} \text{ m}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$. This spread is larger than that observed for corresponding measurements on Markham Clinton groundwater, but does not seem to be associated with a range of particle sizes since SEM measurements suggest that most of the particles are between 50 and 200 nm in diameter. It is possibly associated with a range of particle types. UKNP DLS measurements [LON88] were carried out with the unfiltered water. The measurements were performed for three sampling times (250, 150 and 50 μs) with a Malvern K7025 multibit correlator unit. The graph of the hydrodynamic radius vs sampling time was extrapolated to zero sampling time in order to obtain a value for the average colloid size that is free from interference due to very large particles (5 μm and above). Each point is derived from 10 measurements which were internally consistent, implying that there were no extraneous large particles. Even with these precautions, the resulting size or radius will be biased towards the larger colloids because of their greater scattering power. The average size (diameter) of the particles found by extrapolation to zero sample time is 3 μm (Figure 15).

5.3.2.2 Electron microscopy measurements

UNOS [KRE88] performed TEM tests. From each fluid sample, 5 μl were transferred onto glow discharged mesh grids covered with ultrathin carbon film. The solution surplus was removed, leaving the grids covered with a thin aqueous film which was allowed to air-dry prior to observation in the TEM. Electron-dense particles, approximately 10-20 nm in diameter, were observed in the total sample (Figure 16) as well as in the filtrate (AECL). The concentrate contained more larger phases (200 - 500 nm) (aggregates) as well as small particles of about 40 nm diameter (Figure 16). The increase in the particle size in the concentrate indicates that aggregation took place after the concentration of the sample. The colloid concentration was evaluated for the water sample for sizes larger than $\varnothing_{(m)} = 10 \text{ nm}$. On average, about 50 particles were counted for an area of $4 \cdot 10^5 \text{ nm}^2$. If the colloid distribution on the 3 mm diameter grid ($S_{(act)} = 7 \cdot 10^{12} \text{ nm}^2$) is homogeneous, the colloid concentration in the 5 μl aliquot is about $10^{14} \text{ pt.l}^{-1}$.

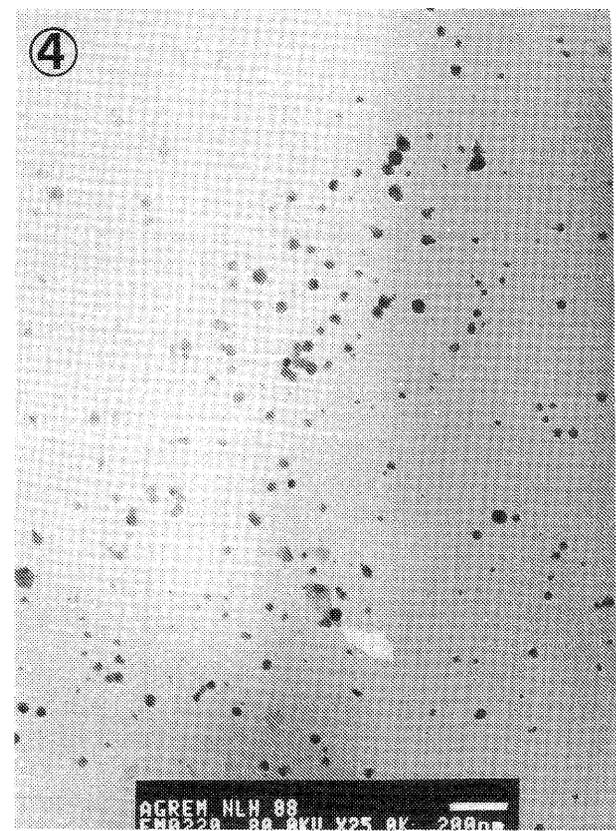
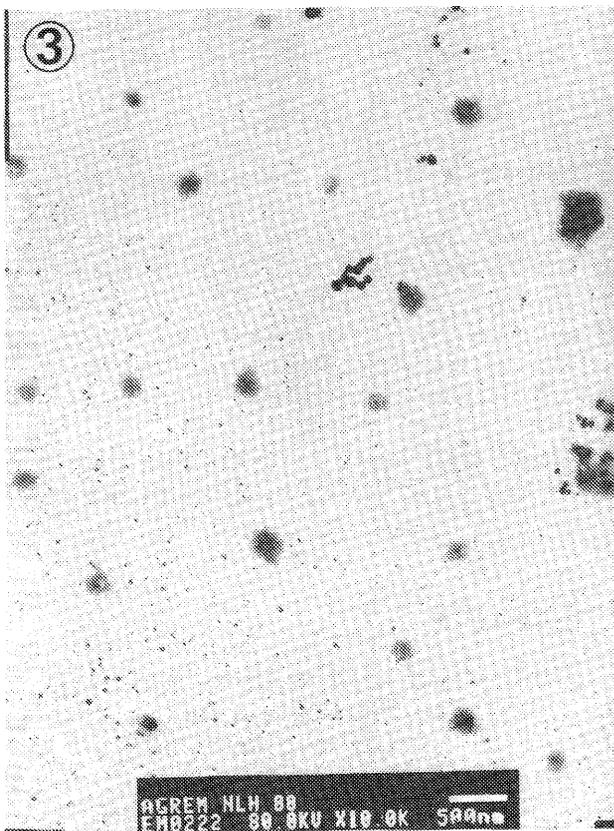
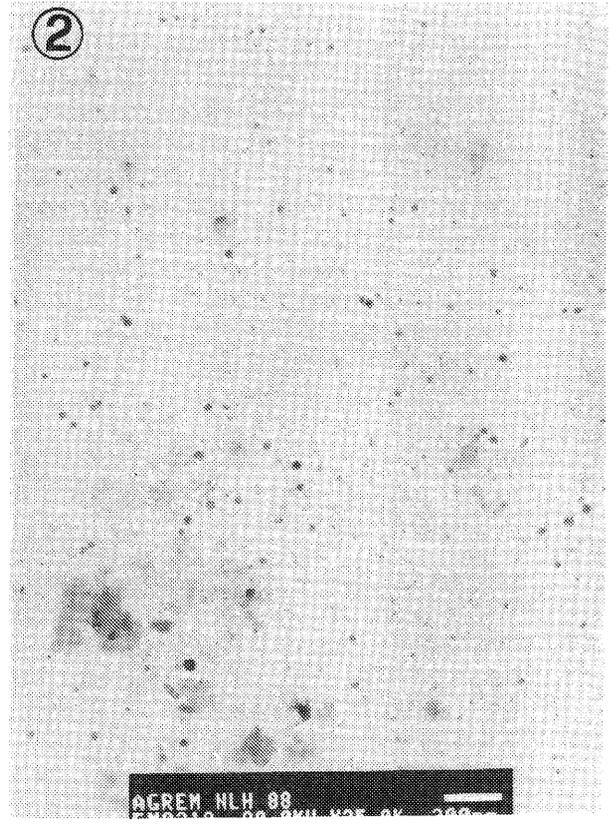


Figure 16: UNOS TEM micrographs of colloids from fluid samples.

- 1- from Grimsel groundwater
- 2- from AECL' filtrate
- 3- from AECL1 concentrate
- 4- from UKNP1 concentrate

5.3.2.3 Chemical and isotopic tests

AECL [VIL88] acidified their samples of filtered Grimsel water and colloid concentrates to 0.12 M HCl prior to U, ^{226}Ra and chemical analysis. Uranium was measured using a Scintrex UA3 laser spectrofluorimeter (LFS) after acidified samples had been neutralized with NaOH. The activity of ^{226}Ra was measured by alpha spectrometry after radium had been extracted from sample solutions with a lead and ^{133}Ba sulphate precipitation technique followed by GNS [SHE85]. Total inorganic carbon (TIC) and total organic carbon (TOC) were measured in non-acidified samples using an Astro 2001 carbon analyser. The composition of filtered Grimsel water and colloid concentrates is summarised in Table 13. Elements associated with colloids are more concentrated in the retentate than in the filtrate. If a significant proportion of an element is associated with large particles, then its concentration is lower in the 1 to 450 nm retentate and higher in the retentate enriched with particles larger than 450 nm. Using the data in Table 13, one can calculate the elemental concentrations of dissolved species, colloids between 1 and 450 nm and particles larger than 450 nm. Si, Ca, Sr and carbonates (TIC) are found mainly in colloids smaller than 450 nm, while Mg, U, and Ra are found in colloids as well as in particles larger than 450 nm. Fe is found only in association with particles larger than 450 nm. Although colloidal organic carbon was found, its size range was not defined due to sorption losses in those samples which were stored in plastic bottles. From these data, the percentage of uranium bound to the colloid is 7.5%.

Table 13: AECL chemical analyses of Grimsel fractionated colloid samples.

The first retentate (>1nm) was concentrated by a factor of 17.5.
The retentate (>450nm) particles are further concentrated 2 times.
The concentrations are given as measured (i.e. not corrected by the concentration factor).

Element		Filtrate/<1nm	Retentate/>1nm	Phase/1-450nm	Retentate2/>450nm
Si	ppm	5.0	7.4	7.5	7.5
Ca	ppm	2.31	20.8	20.7	21.3
TIC	ppm	1.95	6.52	6.56	6.14
Al	ppm	<0.2	<0.2	<0.2	<0.2
Fe	ppm	<0.02	0.126	<0.02	0.179
Mg	ppb	5.6	55	39	63
Sr	ppb	73	630	640	640
^{226}Ra	Bq.l ⁻¹	0.011	0.078	0.064	0.103
U	ppb	0.076	0.212	0.117	0.264
TOC	ppm	0.57	5.20	-	-

BGS [ROS88] analysed the fluid samples by ICP using a Perkin-Elmer Plasma II Emission Spectrometer. All samples were acidified with hydrochloric acid and internally standardised by scandium addition. Chloride, sulphate and bromide were analysed by IC using a Dionex 2000i Ion Chromatograph and fluoride was quantified by direct analysis using an Orion fluoride ion selective electrode. Bicarbonate alkalinity was determined by acid titration. Fluid samples (unfiltered water, UKNP and AECL concentrates) analysed by BGS were all contaminated by air and their pH was about 8. This reduction in pH and an increase in bicarbonate was also measured for all fluid samples at BGS. The other concentrations of interest for the colloidal phase were similar and are compared in Table 19. The difference in composition between the AECL and UKNP colloid concentrates was initially assumed to be due to particulates larger than 1 μm in the AECL colloid concentrate. However, calcium, sodium, strontium, sulphate, total sulphur and fluoride are all a factor of two or more higher in the AECL sample than in either the UKNP concentrate or the groundwater. Lithium, boron, silicon and bicarbonate are also slightly elevated in the AECL sample. This particular enrichment could be due to ion retention [BUF88], the AECL retentate being produced by ultrafiltration through a membrane of smaller cut-off than that used by UKNP. Silicon is the only element found by BGS to have significant enrichment in both concentrates and

the BGS result from the UKNP2 Si analysis is taken into consideration in the discussion. The Si concentration from the AECL sample is not considered because, under the in-situ conditions, silicon is mainly SiO_4H^3 and it may be enriched by salt retention.

Table 14: BGS results for the chemical analyses of fluid samples.

AECL1 concentrate (20.9X), UKNP2 concentrate (38X), unfiltered water analysis by BGS and PSI. The concentrations are given as measured (not corrected by the concentration factor).

Element	AECL1	UKNP2	BGS	PSI
Li	0.100	0.074	0.072	0.085
Na	28.0	16.8	16.2	16.0
Ca	17.5	6.3	6.1	5.7
Sr	0.68	0.176	0.179	0.170
F	12.72	6.67	6.12	6.00
Cl	3.9	1.6	1.5	5.0
Si	7.19	6.32	5.51	5.60
B	0.173	0.092	0.064	0.093
Species				
$(\text{SO}_4)^{2-}$	30.4	7.56	6.61	5.6
$(\text{HCO}_3)^-$	40.1*	34.2*	31.4*	7.3

* equilibrated with air

CEA [MOU88] analysed U in some fluid samples using LFS. In the unfiltered water, the U concentration was 10 - 50 ppt depending on the container (polyethylene - teflon). In the AECL concentrate (20.9X), the concentration of uranium was 130 ppt corresponding to 6 ppt uranium associated with the colloidal phase. This corresponds to between 4 - 25 % U associated with the colloids.

JRC [AVO89] analysed the fluid samples by ICP and chemical analysis. Results converted into enrichment factors (defined as the ratio of an element concentration in a fluid phase to its concentration in the groundwater) are presented together with those of BGS and UNOS in section 6 (Table 20). JRC [BID88] characterised the adsorption behaviour of $^{241}\text{Am}(\text{III})$ on the Grimsel colloids by measuring the sedimentation profiles in ultracentrifuge tubes. A drop of concentrated $^{241}\text{Am}(\text{III})$ solution was dried and re-dissolved with an aliquot of Grimsel groundwater with pH adjusted to 6.5: comparison with literature data showed namely that the final Am concentration was below the solubility limits of $\text{Am}(\text{OH})_{3(s)}$, $\text{Am}_2(\text{CO}_3)_{3(s)}$ and mixed hydroxy-carbonate species at that pH. After equilibration for three weeks, the solution was passed through a filter of $0.22 \mu\text{m}$ pore-size. $10 \mu\text{l}$ were then added to 32 ml of water samples in ultracentrifuge tubes. These water samples consisted of unfiltered water, AECL concentrate (X20.9), AECL ultrafiltrate and UKNP concentrate (X28). The Eh value (Table 4) measured in the groundwater sample after dispatching was positive and all the experiments were carried out under normal laboratory atmosphere. Spiked solutions were kept two weeks in cold, dark conditions and stirred gently every second day. After this period, the four solutions were ultracentrifuged for 110 hrs at 28,000 rpm ($\omega^2 t = 3.43 \cdot 10^{12} \text{ rad}^2 \cdot \text{s}^{-1}$). After centrifugation, 20 samples of about 1.5 ml were carefully extracted, starting from the top of the solution, and measured for the ^{241}Am content (Table 15). In parallel, water samples without centrifugation were measured in order to correct for Am adsorption on the tube walls. Similar experiments were carried out with a reduced centrifugation time of 14 hrs at 28,000 rpm ($\omega^2 t = 4.18 \cdot 10^{11} \text{ rad}^2 \cdot \text{s}^{-1}$). In both ultracentrifugation series, it was seen that Am colloids collected mainly at the bottom of the vessel. Although colloids may stick to the bottom of the tube, profiles through the fluid were determined. JRC found that iron was also concentrated at the bottom of the centrifuge tube.

Table 15: JRC measurements of ^{241}Am -Fe associated Grimsel colloids.
 Profile of Am-Fe after centrifugation ($\omega^2 t = 3.43 \cdot 10^{12} \text{ rad}^2 \cdot \text{s}^{-1}$);
 values are given in % of their initial concentrations prior to
 separation; each fraction is about 1.5 ml. nd: non detectable.

	Groundwater		AECL1		AECL'		UKNP1	
	Fe ppb	Am M	Fe ppb	Am M	Fe ppb	Am M	Fe ppb	Am M
Initial concentration	<2	$4 \cdot 10^{-10}$	4.2	$4 \cdot 10^{-10}$	<2	$3 \cdot 10^{-10}$	3.3	$2 \cdot 10^{-10}$
After UF Fraction	%	%	%	%	%	%	%	%
1	nd	33.2	nd	57.7	nd	73.7	nd	35.3
2		36.6		59.5		76.6		30.3
3		35.7		60.2		73.7		34.7
4		38.1		60.0		74.5		32.8
5		36.9		57.9		72.6		35.4
6		38.3		58.4		73.3		31.8
7		37.4		63.5		75.0		34.6
8		38.8		60.3		75.6		32.1
9		35.5		61.1		72.2		35.0
10	nd	37.1	nd	63.7	nd	74.8	nd	35.6
11		35.7		58.8		72.5		34.7
12		35.5		63.9		71.9		39.7
13		38.0		62.1		71.5		40.0
14		38.1		61.7		73.0		37.9
15		37.7		61.7		73.9		38.4
16		37.2		64.6		73.2		35.7
17		37.1		63.9		78.0		41.2
18		38.9		62.4		76.5		41.8
19		40.0		61.1		117.2		34.6
20	nd	97.8	94.5	126.5	nd	960.5	78.5	215.9

KUL attempted CEC measurements on AECL3 using the silver-thiourea test [CRE73]. However, the test failed, perhaps because it was below the detection limit ($10 \mu\text{M}$) or, as suggested, because the colloids are oxides, in which case the technique is not applicable.

PSI performed total organic carbon (TOC) measurements on the fluid samples. These tests were performed with a Dohrman carbon analyser. TOC concentrations (average of 2 measurements) are reported in Table 16. Due to the low TOC concentration, ($<1\text{ppm}$) these results are to be treated with caution (sorption onto vessel and contamination problems). Colloidal organic carbon (COC) defined from the concentrate (UKNP) content is about 2 ppb but, from the difference between the unfiltered water and the AECL ultrafiltrate, COC is 64 ppb. The TOC in the AECL concentrate is lower than in the UKNP concentrate because, as noticed by AECL, a proportion of the organic material was sorbed by the plastic container. CEC tests were carried out at PSI by copper sorption and potentiometric titration [BUF77] on AECL2 and AECL'. Here again the test was below its detection limit ($2 \mu\text{M}$). In addition, sorption tests on AECL2 with cobaltihexamine [STU76,DAL77] were below detection limit ($0.5\mu\text{M}$). Additional tests carried out with AECL3 were close to the detection limit. PSI evaluation of U associated with natural colloids was carried out before the exercise by counting (ANS) membranes such as PSI5 for 200 h. The specific activity of ^{238}U on the 3 nm membrane was below 0.1 mBq per litre of groundwater (i.e. $< 8 \text{ ppt}$).

Table 16: PSI total organic carbon results.

Sample description	container	TOC/ppb
AECL ultrafiltrate	plastic/teflon	163.4 ± 1
AECL concentrate	plastic/teflon	230.9 ± 2
PSI unfiltered water	teflon	227.2 ± 9
PSI milliQ water	teflon	121.8 ± 19
UKNP concentrate	glass	281.2 ± 8
PSI unfiltered water	glass	192.6 ± 3
PSI milliQ water	glass	102.2 ± 12

UKNP [LON88] performed uranium series measurements with the fluid samples. Both the prefilter and the ultrafilter were treated with acid to leach out the adsorbed or trapped activity. The fluid samples were acidified with nitric acid to inhibit plating-out of uranium and thorium and spiked with ^{236}U and ^{229}Th . Iron carrier was added and the sample reduced in volume by boiling to about 1 l. Uranium and thorium were coprecipitated with ferric hydroxide by addition of ammonia and separated using ion-exchange columns. The dry fraction was then electroplated onto stainless steel planchets to produce sources which were counted for periods in the order of 2 - 4 10^5 s. Actinide activities are presented in Table 17 together with the actinide levels in the blank. The total activity (Bq) for each phase was calculated for the known volume of groundwater passing through the Amicon rig and that for the colloid fraction was obtained from the activity on the colloid concentrate minus that in the same volume of ultrafiltrate. The ratio $^{234}\text{U}/^{238}\text{U}$ found here for the filtered water is $1.52(\pm 0.30)$, corresponding to preferential leaching of ^{234}U in the mylonite system. The ratio for the particles is $1.57(\pm 0.69)$, which is the same as for the unfiltered water, and could be due to the acid desorption of uranium in the prefilter. For the colloids, the uncertainty is so large that nothing definitive can be concluded. For the sake of comparison, the isotopic ratios measured for the mylonite (AU126) are given by [ALE88]. He found $^{234}\text{U}/^{238}\text{U} = 1.02(\pm 0.06)$ and $^{230}\text{Th}/^{234}\text{U} = 1.08$. In this zone, however, the absence of groundwater avoid modification of the radiochemical equilibrium.

Table 17: UKNP natural actinide analysis in colloid fractions and a blank.

Errors are calculated from the counting.

Sample	specific activity/mBq.kg ⁻¹ and actinide partitioning/mBq and %				
	^{238}U	^{234}U	^{230}Th	^{232}Th	^{228}Th
-					
Prefiltered water	167±33	250±50	150±30	20±20	50±50
UKNP2	370±80	530±120	550±180	180±120	150±180
Ultrafiltrate	320±30	480±50	120±20	100±50	130±20
Prefilter wash	5±1	8±2	7±1	0.7±0.4	0.3±0.1
Ultrafilter wash	116±7	126±7	8±1	0.6±0.5	2±1
Blank	0.07±0.12	0.0±0.05	0.07±0.08	0.00±0.05	0.2±0.05
>1 μm particles	0.70±0.17	1.10±0.22	1.00±0.18	0.10±0.05	0.03±0.20
%	1.1±0.3	1.2±0.2	4.8±0.9	0.7±0.4	0.2±1.2
Colloid 2nm-1μm	0.23±0.37	0.23±0.55	1.80±0.78	0.30±0.50	0.03±0.33
%	0.4±0.6	0.3±0.7	8.8±3.8	2.4±3.4	0.2±2.2
Ultrafilter	16.6±0.9	18.0±1.0	1.1±0.2	0.08±0.07	0.3±0.2
%	26.4±1.5	20.4±1.1	5.5±1.0	0.5±0.4	1.5±0.9
Ultrafiltrate <2nm	45.2±4.8	68.9±6.8	16.6±2.3	14.3±2.4	19.0±2.3
%	72.1±8.0	78.1±8.0	81.0±11.0	96.0±16.0	98.0±12.0

UNAN [PIE88] studied the unfiltered water sample. Since the sample was too dilute to be studied directly by UC in a sucrose gradient (0-15%), dialysis was carried out with a Microprodicon apparatus. The membranes were Prodimem PA-10 with a cut-off of 10,000 mwu, and the dialysis was performed over 72 hours in order to enrich the sample by a factor of 60. The 220 - 700 nm spectrum of this concentrate was recorded (Figure 17). It presented a peak at 257nm, comparable to those reported for some organics [GIL62,MOU86]. This absorbance (blank corrected) corresponded to a concentration of about 80 ppb COC. The final concentration obtained after dialysis was, however, too low to allow estimation of the molecular weight by UC in a sucrose gradient.

UNOS [SAL81, SAL85a+b] utilised instrumental neutron activation analysis (NA) for trace element determination and inductively coupled plasma emission spectroscopy (ICP) for major element determination in the fluid samples. For NA, aliquots of approximately 4 ml were transferred to quartz ampoules and weighed accurately before heat sealing. The samples plus multielement standard solution were irradiated for 3 days with a neutron flux of $1.5 \cdot 10^{13} \text{ n.s}^{-1}.\text{cm}^{-2}$. The samples were transferred to counting vials and measured after decay times of 3, 10 and 30 days. The enrichment factors for the fluid samples are reported in Table 20 together with other information. Results for Mg, Ca, B and Al are based on ICP while the others are determined by NA. UNOS detected Zn contamination in the fluid samples stored in polyethylene bottles. In addition, Al speciation was carried out in both AECL1 and AECL' samples using the Barnes/Driscoll technique [BAR75,DRI84]. In the ultrafiltrate, the concentrations of both acid reactive Al and monomeric reactive Al were 13 ± 4 and 9 ± 1 ppb respectively. The species concentrations for the concentrate are not reported here because of the artefact problem discussed in section 6. However, the results indicate that Al is present in neutral or negatively charged forms in the ultrafiltrate and predominantly as colloids in the concentrate.

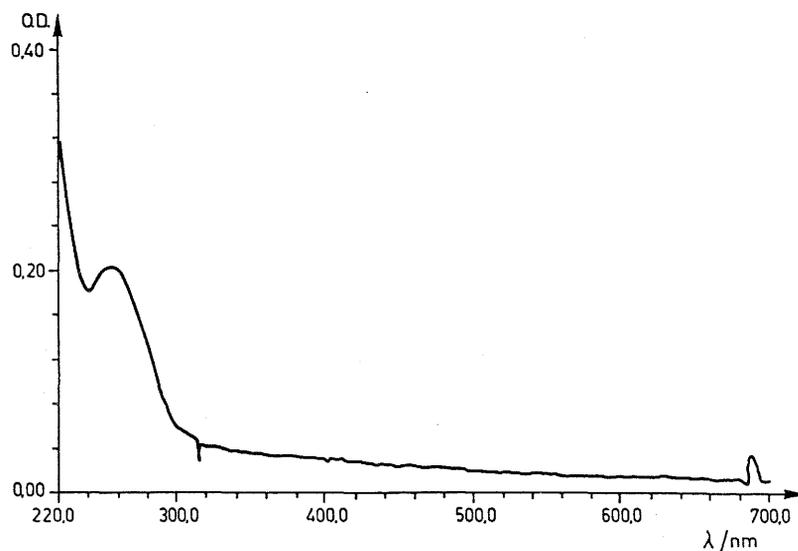


Figure 17: UNAN UV/VIS spectrum of a colloid dialysis concentrate.

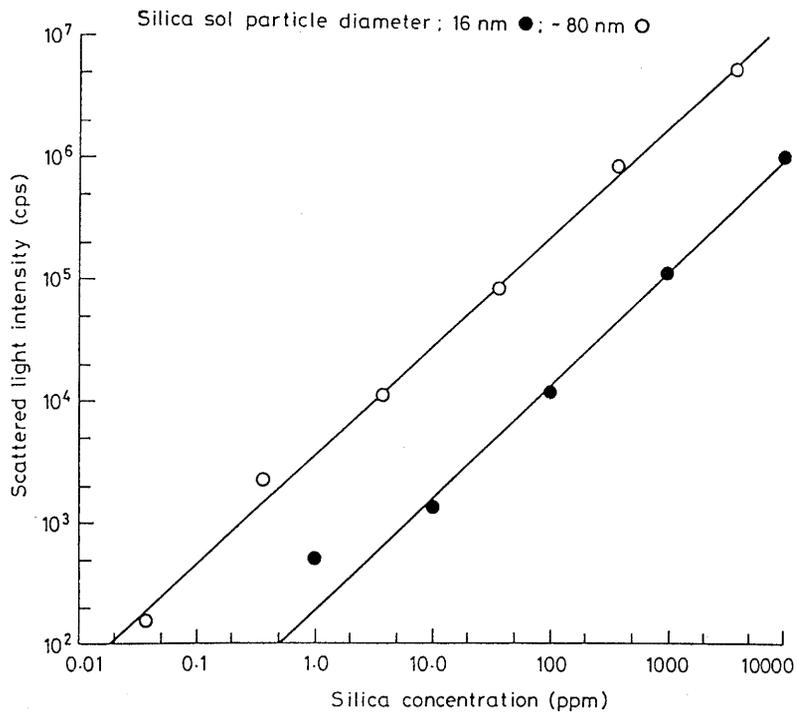


Figure 18_a

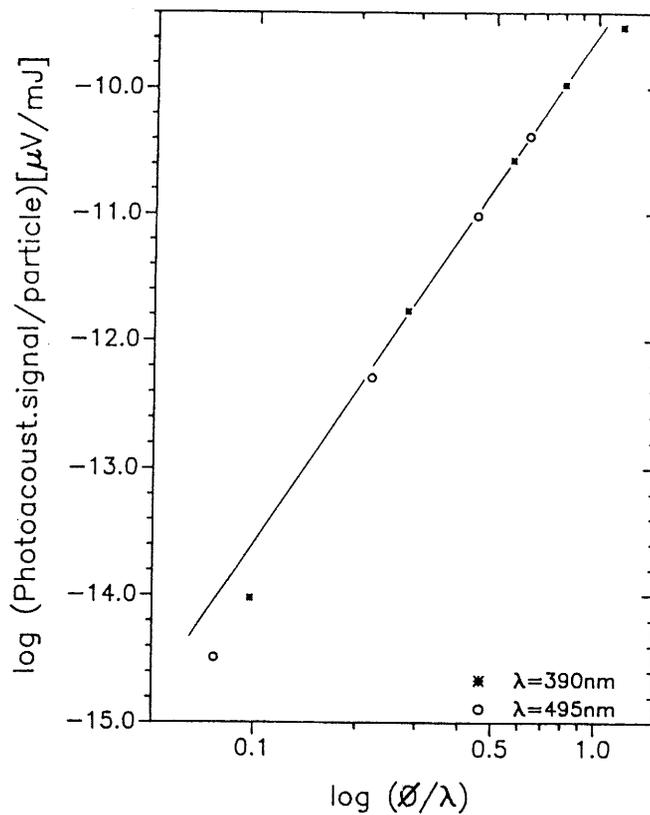


Figure 18_b

Figure 18: a. UKC static light scattering and
 b. TUM laser-induced photoacoustic spectroscopy calibration curves.

6 INTERCOMPARISON OF THE RESULTS AND DISCUSSION

Assorted data on colloid concentration, size distribution and chemical composition are discussed in this section. Calibration tests with model or "standard" colloids are also documented. These colloids were used to calibrate some techniques, but the same standard has not been used to check all the analytical techniques discussed. The intercomparison is based on the scheme discussed at the Grimsel Colloid Exercise Workshop, PSI, Wurenlingen on July 13, 1988 [DEG88b]. It can be summarised as follows.

In order to compare results obtained by microscopic and gravimetric techniques, an equation allowing conversion from particle to mass units is used based on the hypothesis of spherical colloids.

$$\frac{\delta[\text{coll}]}{\delta\emptyset} / \text{g.l}^{-1}.\text{nm}^{-1} = \frac{\rho.\pi.\emptyset^3}{6} \cdot \frac{\delta[\text{coll}]}{\delta\emptyset} / \text{pt.l}^{-1}.\text{nm}^{-1} \quad [6.1]$$

This conversion is made with an assumed average density ρ of $2 \cdot 10^{-21} \text{ g.nm}^{-3}$.

The specific size distribution $\log\{\delta[\text{coll}]/\delta\emptyset\}=F(\emptyset)$ is a useful function for the modeller since it can be used to evaluate different relevant parameters such as the diffusion coefficient and the CEC on the basis of site/active group surface density. The diffusion coefficient D is namely related to \emptyset by the Stokes-Einstein relationship:

$$D = \frac{kT}{3\pi\eta\emptyset} \quad [6.2]$$

where k is the Boltzmann's constant and η the groundwater viscosity.

The CEC can be calculated as corresponding to surface site capacity $\text{CEC}_{(m)}$ or the capacity of a nanoporous colloid $\text{CEC}_{(M)}$. The site density ϵ in model material ranges from 1 to about 10-20 sites nm^{-2} [JAM82] and an average of 3 sites nm^{-2} and nm^{-3} respectively was chosen for the purpose of this work. Hence, we have

$$\text{CEC}_{(m)} = \int_{\emptyset_{(m)}}^{\emptyset_{(M)}} \frac{\epsilon.\pi.\emptyset^2}{N_{(Av)}} \cdot \frac{\delta[\text{coll}]}{\delta\emptyset} \cdot d\emptyset \quad [6.3]$$

and

$$\text{CEC}_{(M)} = \int_{\emptyset_{(m)}}^{\emptyset_{(M)}} \frac{\epsilon.\pi.\emptyset^3}{6.N_{(Av)}} \cdot \frac{\delta[\text{coll}]}{\delta\emptyset} \cdot d\emptyset \quad [6.4]$$

where $N_{(Av)}$ is the Avogadro constant and ϵ the site density in nm^{-2} or nm^{-3} according to the selected hypothesis. The CEC is reported in mole.l^{-1} and for the fluid sample.

LPAS [KLE86] results were first quantified by comparing the groundwater photoacoustic signals with the LPAS spectra of 0.1 to 50 ppm latex solutions. The photoacoustic signals, corrected for the signal of pure water and energy losses in the cuvette at higher extinction, are found to be proportional to the extinctions of these solutions as determined by transmission spectroscopy. Figure 18 presents the calibration curve used for LPAS test quantification. As the absorption of the latex in the 380, 475 and 840 nm spectral ranges is negligible, the photoacoustic signal is expected to be proportional to the concentration of scattering particles. This effect is not theoretically based. However, these results allow partial quantification of the colloids in the groundwater. On the assumption that the scattering of the groundwater colloids is similar to that of 220 nm latex beads,

Size distribution of SiO₂ (Quartz), 10 ppm.

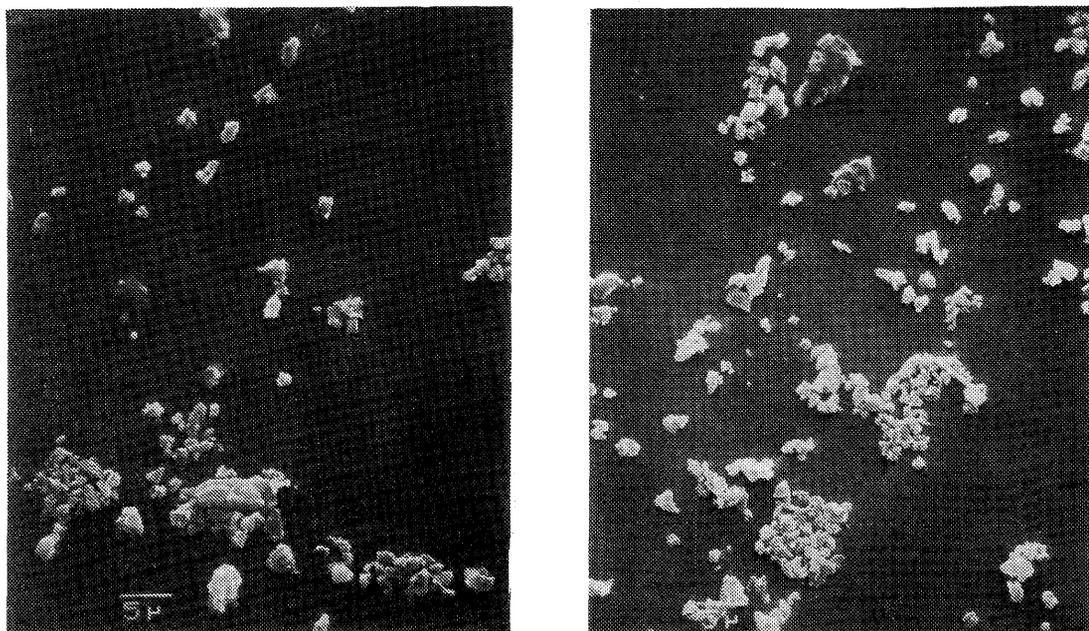
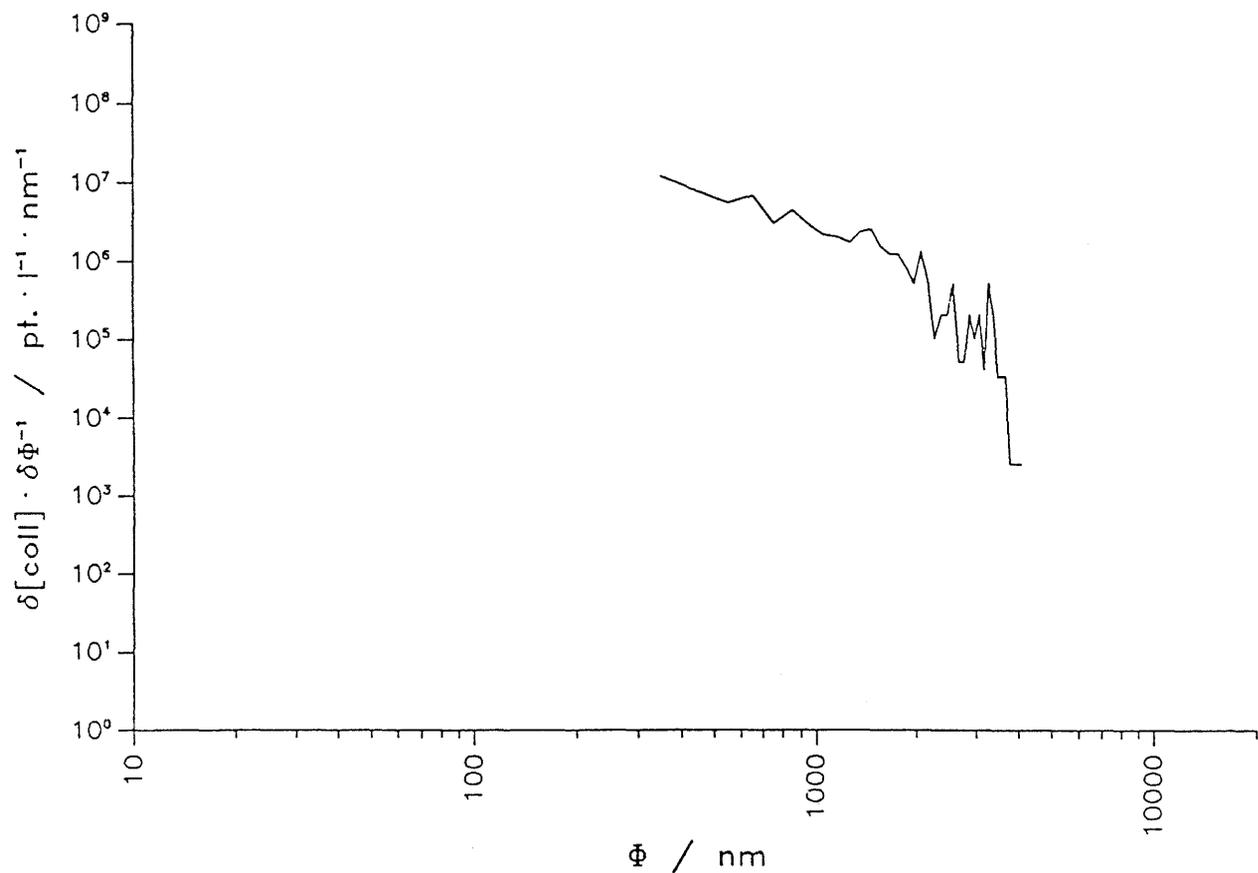


Figure 19: PSI UF/SEM calibration with standard colloidal quartz.

the approximate colloid concentration can be evaluated. Ignoring differences in size distribution as well as in density of the particles, calculations from the photoacoustic signal at 370 nm and the slope in this region give rise to a total Grimsel colloid concentration of $6 \cdot 10^9$ pt.l⁻¹. Finally, LPAS spectra before and after UF seem to indicate the presence of very small colloids which are difficult to separate from the fluid phase or, alternatively, this colloid population is re-formed after separation.

PSI calibration of the combination of PDUF and SEM was carried out with an EC standard colloid material (quartz). A 10.0 ± 0.1 ppm colloidal quartz solution was filtered through a 3 nm membrane which was prepared for SEM investigation. Figure 18 presents two typical micrographs and the colloid specific size distribution for this solution. The minimum size is, as certified, 0.35 μ m and the maximum class is 3.5 μ m. The colloid concentration expressed in mass is compared with that obtained using the AECL gravimetric approach for a 10 ppm solution in Table 18. It can be seen that the agreement is satisfactory. It should be noted that the colloid concentration used (in pt.l⁻¹) is of the same order of magnitude than that of the Grimsel groundwater.

Table 18: Comparison of AECL MF/GRAV and PSI UF/SEM results for a 10 ± 0.1 ppm colloid solution of EC quartz standard.

[coll]/ppm	[coll]/ppm GRAV	[coll]/ppm SEM	[coll]/pt.l ⁻¹
10 ± 0.1	9.8 ± 2.1	14.5 ± 5.0	$6.1 \cdot 10^9$

Conditions: AECL/GRAV methodology with a single MF (0.1 μ m) and 2 tests, PSI/UF/SEM with 4 micrographs (10,000X) of the 3 nm pore-size polyacrylamide membrane. BRM certified size of standard colloid: 0.35 - 3.5 μ m.

GRAV results (Tables 9 and 11) indicate that, for the separation performed in-situ, the particle concentration (0.24 ppm) is 5 times smaller than that obtained after separation performed in the laboratory with shipped groundwater (1.16 ppm). This could be due to contamination (glass or stopper leaching or bacteria) or due to the fact that the in-laboratory separation is performed under a nitrogen atmosphere allowing calcite to precipitate, while the on-site separation involves air contamination allowing calcite (generated by ion retention) to be dissolved.

The AECL chemical analysis of the Grimsel colloid concentrates indicates that colloids in Grimsel waters are mostly smaller than 450 nm. If the concentrations of all the colloidal elements are combined, they give a colloid concentration of about 2.7 ppm, or 0.5 ppm without calcite (Table 19). The GRAV results show the concentration of particles greater than 10 nm to be 0.24 and 1.16 ppm (with or without air contact respectively). If one assumes that the aerobic contamination eliminates calcite colloid, then comparing the 0.5 ppm (>1.5 nm) result obtained by analysis of the fractions and the 0.24 ppm (>10 nm) obtained with the GRAV methodology, one could explain the variation by the difference in the minimum fraction size. During the AECL colloid concentrate production, salt may have been retained in the concentrate. Although the 10,000 molecular weight membranes are not expected to retain salt by reverse osmosis, the retention of dissolved Cs, Sr and I tracers has been observed, particularly when high transmembrane pressures are used [VIL89]. The enrichment of calcium and carbonate may have led to the formation of carbonate complexes or the precipitation of carbonate colloids. Table 19 shows that calcite solubility was exceeded when the colloid concentrate was produced without contact with atmospheric CO₂. The creation of carbonate complexes or colloids would have further enhanced the retention of Ca, Mg, Sr, Ra and possibly other cations or anions. If these colloids (or complexes) were smaller than 10 nm they would not be detected by GRAV methodology. However, air contamination increases the TIC and, with the pH drop, calcite is dissolved.

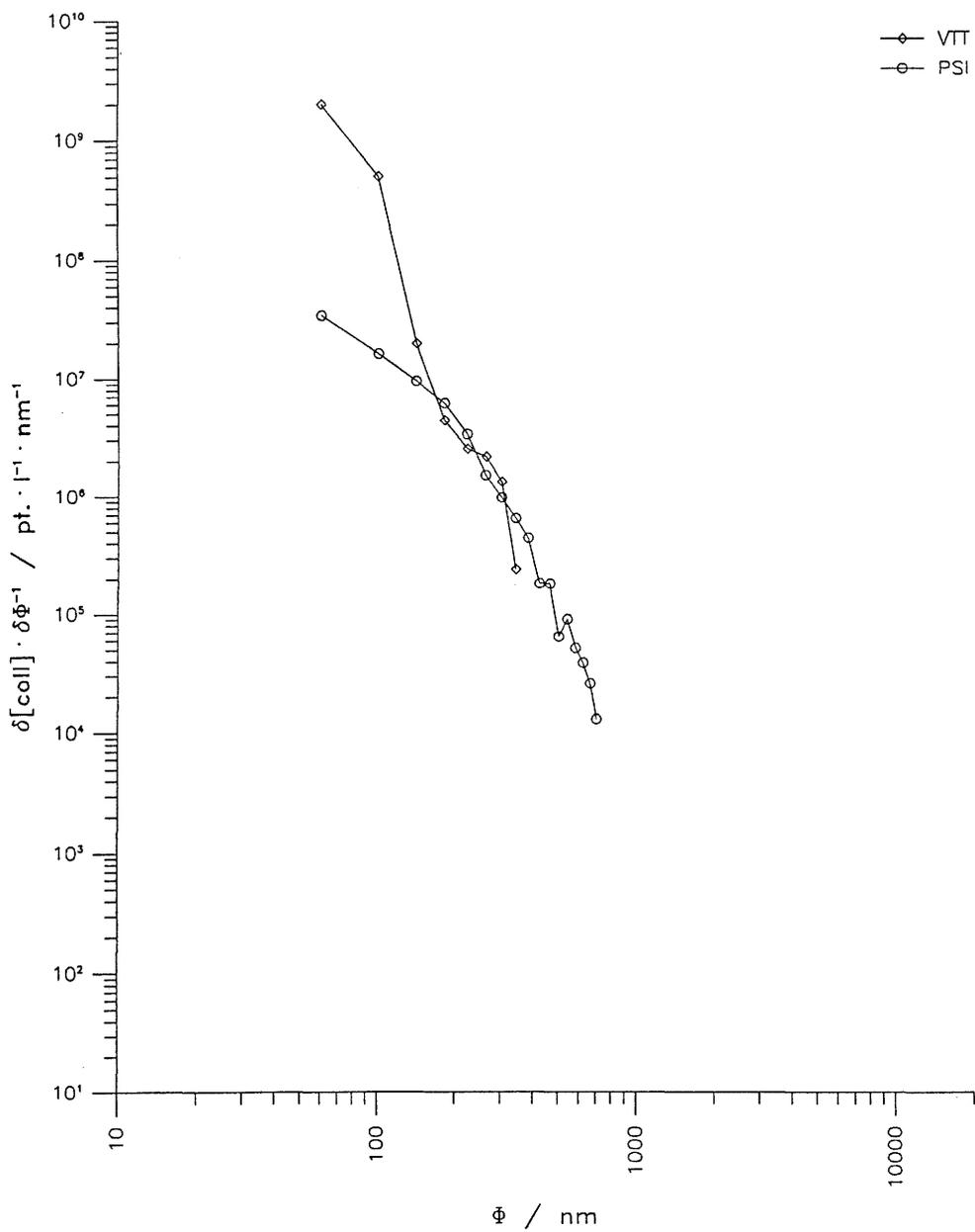


Figure 20: Comparison of VTT and PSI specific size distribution for PSI5.

Table 19: Comparison of saturation indices calculated for groundwater and the AECL concentrate.

Elem./Spec.	Data/groundwater	data/concentrate -->	data/equil. air
pH	9.6	9.6	8.4
log P (CO ₂)	-5.5	-5.2	-3.7
Na	16.0 ppm	28.0 ppm	
Ca	5.7 ppm	20.8 ppm	
Si	5.6 ppm	7.4 ppm	
Mg	13.- ppb	55.- ppb	
Sr	161.- ppb	630.- ppb	
Cl	5.0 ppm	13.- ppm*	
F	6.0 ppm	12.7 ppm	
(SO ₄) ²⁻	5.6 ppm	30.4 ppm	
TIC	3.9 ppm	6.5 ppm	9.3 ppm
Fe	50.- ppb**	126.- ppb	

Chemical spec.	Ref.	SI/Groundwater	SI/AECL concentrate -->	SI/equil. air
Calcite	[PLU82]	0.00	0.74	-0.20
Dolomite	[PAR80]	-2.45	-0.98	-2.88
Strontianite	[BUS84]	-0.97	-0.24	-1.20
Gypsum	[LAN85]	-3.66	-2.47	-2.45
Anhydrite	[LAN85]	-4.15	-2.96	-2.94
Celestite	[LAN85]	-3.45	-2.22	-2.22
Fluorite	[SMI76]	-0.40	0.74	0.76
Chalcedony	[FOU81]	-0.06	-0.32	-0.16
Quartz	[FOU81]	0.41	0.11	0.27
Fe(OH) ₃ (Amorph)	[BAE76]	2.77**	3.17**	-

Remarks: * for the AECL concentrate Cl is estimated according to the enrichment factor, but the analysis does not charge balance (~5% excess of ions).

At pH = 8.4, log P (CO₂) = -3.7, calcite is saturated (i.e. nearly in air atmosphere conditions). Calculation with code PHREEQE [PLU82] and with Eh = 0 mV for both fluid sample kept in anaerobic condition.

**conservative value.

Ion retention is, however, evident when taking into account the enrichment factors defined as the ratio of concentration in fluid phase to that in unfiltered water. Enrichment factors measured by BGS, JRC and UNOS are reported on Table 20. The agreement between analyses is rather good. They show that species which should not belong to the colloidal phase such as Cl, Br, F and lesser S (as sulfate) are enriched in the retentate and depleted in the filtered phase. This enrichment is stronger when the cut-off is decreasing from 2.1 nm for the UKNP samples to 1.5 nm for the AECL one. Cation such as Li, Na, Ca, ... are also enriched in the concentrate. The colloid concentrations derived from these data yield to over-estimated values because ion retention takes place. On the basis of PHREEQE calculations iron should be present in the original water mainly as Fe(III) and should be stabilised at this valence state by the hydroxyl ion yielding an Fe(OH)₄⁻ complex. PHREEQE calculations indicate that the concentration of this complex is $8.8 \cdot 10^{-7}$ M in groundwater, while the concentration of the predominant form of Fe(II), (FeOH)⁺, is $9.3 \cdot 10^{-11}$ M. However, these calculations depend on assumed redox, the data base used and on the presence of trace of DOC.

Figure 21_a

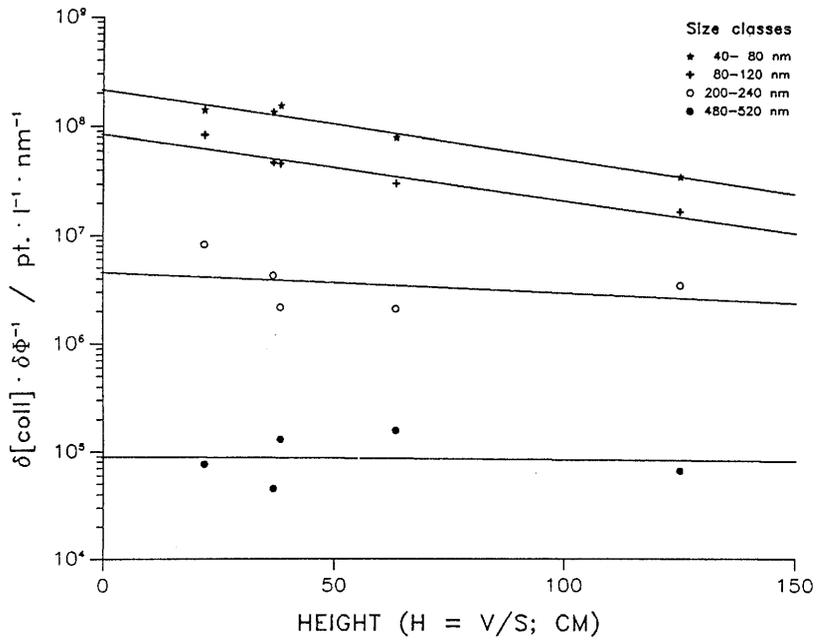


Figure 21_b

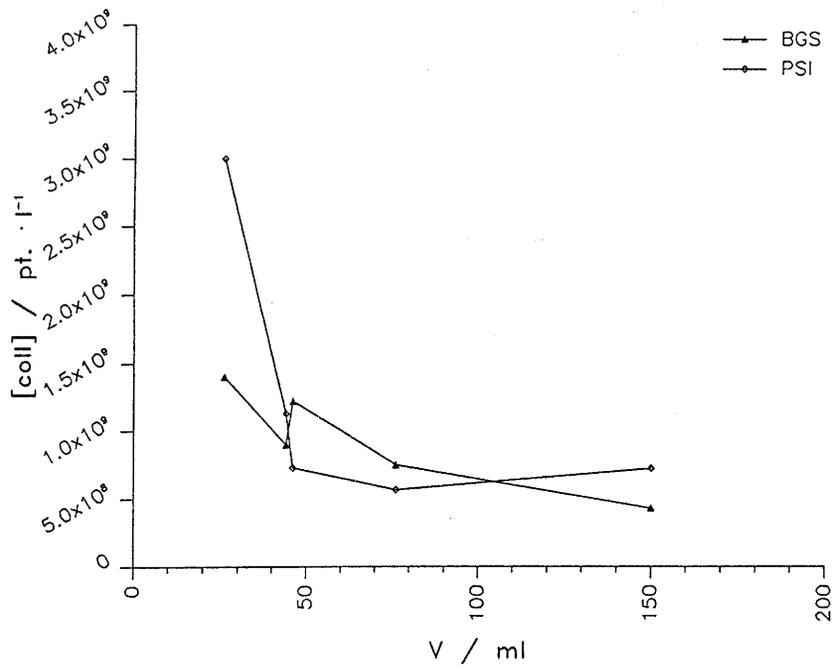


Figure 21: a. PSI filtration geometry study
 b. comparison of BGS and PSI colloid concentration as a function of filtered volume.

Table 20: Comparison of reported enrichment factors for fluid samples.
Concentration factor relative to unfiltered groundwater.

Sample Analysis	UKNP1			UKNP2			AECL1			AECL'	
	BGS	JRC	UNOS	BGS	JRC	UNOS	BGS	JRC	UNOS	JRC	UNOS
Li	1.03	1.1	-	1.39	1.6	-	1.0	-			
B	-	0.9	1.2	-	2.2	1.2	0.6	1.0			
F	1.09	1.28	-	2.08	2.5	-	0.86	-			
Na	1.04	1.15	1.2	1.73	1.77	1.7	0.74	0.8			
Mg	-	1.75	1.0	-	10.-	2.0	0.21	0.8			
Al	-	1.7	1.0	-	4.7	2.2	0.6	0.6			
Si	1.15	1.30	-	1.30	1.31	-	0.88	-			
S (SO ₄ ²⁻)	1.14	-	-	4.60	-	-	-	-			
Cl	1.07	1.21	-	2.60	1.83	-	0.75	-			
Ca	1.03	1.09	1.0	2.87	2.97	2.4	0.40	0.7			
Sc	-	-	4.3	-	-	2.2	-	0.6			
Cr	-	-	3.6	-	-	2.4	-	0.8			
Fe	-	-	2.2	-	2.1	3.3	-	0.7			
Co	-	-	2.4	-	-	3.0	-	0.8			
Br	-	-	1.0	-	-	1.2	-	0.9			
Sr	0.98	1.08	1.0	3.80	3.85	3.9	0.66	0.7			
Sb	-	-	1.0	-	-	2.0	-	0.8			
Cs	-	-	1.0	-	-	1.3	-	0.8			
Ce	-	-	3.1	-	-	7.1	-	0.6			

The concentrations derived from the chemical analysis of the AECL fractions should be corrected by the concentration of the phases obtained by enriching colloid free solution or synthetic groundwater in the same conditions. Another important source of interference is the sorption of organics, not only on the plastic vessel as reported by AECL but also on the membrane itself as observed at PSI [VIL89]. This phenomenon is visible with the flat membrane system because it can be opened after filtration but cannot be directly checked for the hollow fibre unit. Therefore, the data obtained by difference between the filtrate and the unfiltered water are probably more realistic than those obtained from direct analysis of the concentrate analysis.

The UNAN UVS result translated from DOC concentration according to the correlation described by [BUF82] yields 80 ± 40 ppb of C as colloidal organic material.

The bacteria concentration is about 10^6 l⁻¹ and, with an average size of $1 \mu\text{m}^3$ and a density of 1 g.cm^{-3} , these bacteria correspond to a bioorganic concentration of about 1 ppb.

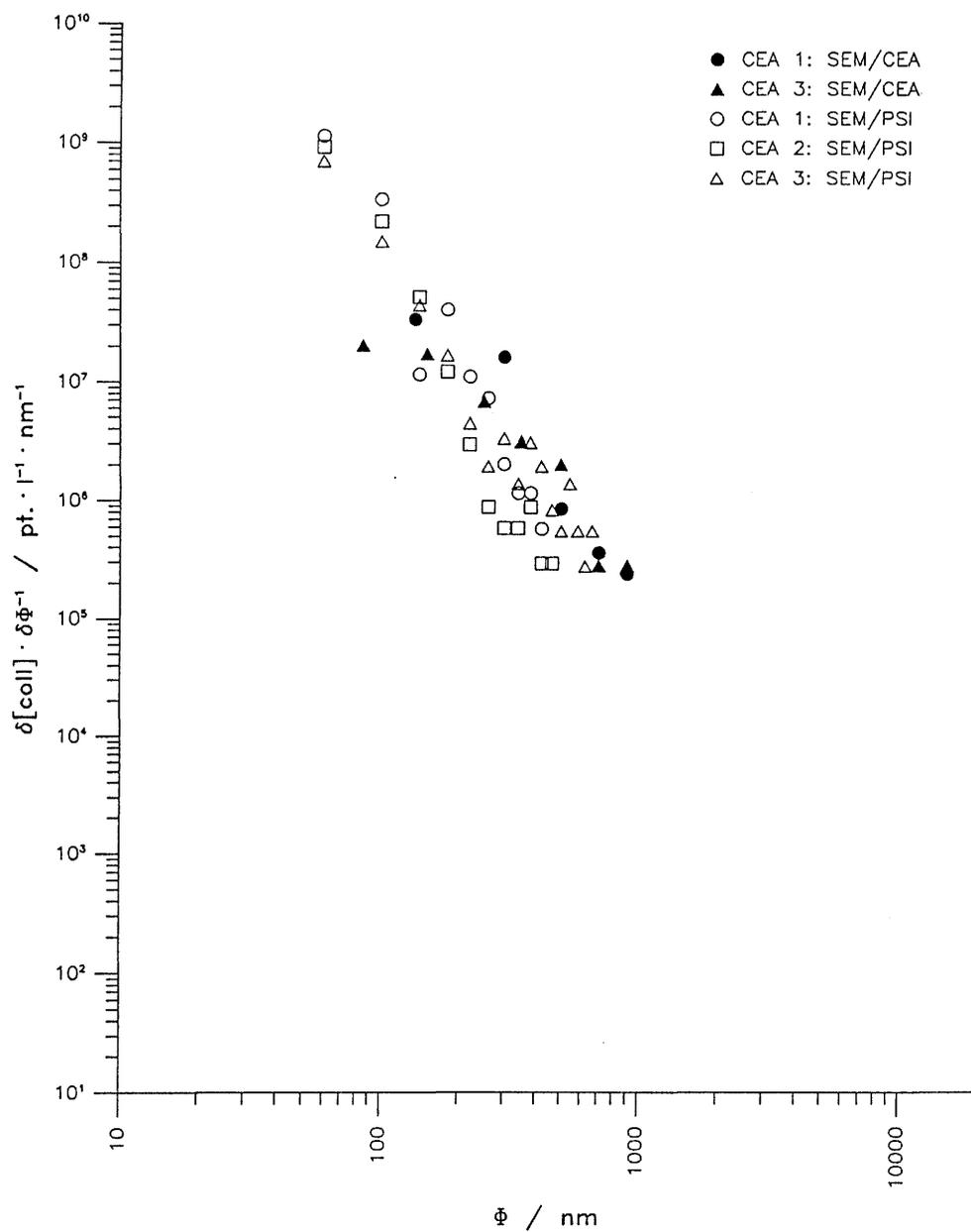


Figure 22: CEA and PSI specific size distribution comparison for CEA1-3 samples.

Table 21: Comparison of colloidal concentration (in ppm) obtained by chemical analysis (AECL, BGS, PSI), UVS (UNAN), SLS (UKC), LPAS (TUM) and GRAV (AECL).

Colloidal material	AECL	BGS	PSI	UNAN	UKC	TUM	GRAV/AECL
COC	0.22-0.26		0.002-0.064	0.08			
organic	0.44-0.52		0.005-0.130				
SiO ₂	0.29-0.30	0.046-0.172					
Sr	0.03						
Mg	0.003						
-----	-----	-----	-----	---	-----	-----	-----
Total*	0.73-0.85		0.05-0.30		0.2	0.095#	Total* 0.24
Ca	1.06						
(CO ₃) ²⁻	1.10-1.31						
-----	-----						-----
Total**	2.89-3.22						Total**1.16

Total* without calcite

Total** with the calcite generated during separation.

average density assumed: 1.

Organic 50% COC on basis of the average composition of humic material [GRA88].

UKC measurements with SLS indicate the adsorption (concentration decrease) of colloids on the plastic container or their retention on the membrane surface, causing a lower count (Table 12) compared to the result obtained with the glass bottle. The effect of air contamination is negligible in the SLS counting. Inorganic and organic colloids and the glass surface are supposedly negatively charged for pH ranging from 8.0 to 9.6, increasing the repulsion between phases. Nothing is known about the charge of polyethylene in contact with the Grimsel water. PSI particle counting results (Figure 14) present a similar trend, with the specific size distribution of the water stored in the polyethylene bottle being smaller than that for the glass bottle. Depletion of key elements such as Fe and Al, as observed by CEA (section 5.1.2), also indicates storage losses of these elements in the plastic containers.

For an evaluation of the SLS results [NIC88], a calibration of the count rate as a function of particle concentration from two silica sols types was measured. These colloids had nominal particle diameters of 16 and 80 nm respectively. Figure 18_a shows the calibration curves. For the Grimsel samples, a scattering intensity of 1000 cps (above background) corresponds to silica concentrations of 4 and 0.2 ppm respectively for the two diameters. These mass concentrations are equivalent to particle concentrations of 10¹⁴ and 10¹¹ particles per litre, assuming a silica density of 2.2 g.cm⁻³. Because the MF/SLS test indicates that the size of the colloid counted is somewhat larger than 0.1 μm, UKC suggests tentatively that the particle concentration in the natural polydispersed sample is about 10¹⁰ pt.l⁻¹.

TUM improved the LPAS measurements by detecting scattered light directly on a piezocrystal transducer. The time difference in signal propagations between photoacoustic waves and scattered light allows quantification of the colloid population, provided the average size distribution of colloids is known. This method is being developed further. The preliminary quantification result for Grimsel water reported for an average diameter of 100 nm is 0.095 ppm. The calibration was done by measuring latex solutions of different concentrations with various particle diameters (40-300 nm). The density of colloids is assumed to be one and the total particle number counted in the Grimsel water by LPAS is 4.2 10¹¹ pt.l⁻¹.

The comparison of VTT and PSI counting for the PSI5 sample is illustrated in Figure 20. It shows a difference in colloid counting for $\varnothing < 0.1 \mu\text{m}$. Manual counting is perhaps more accurate because

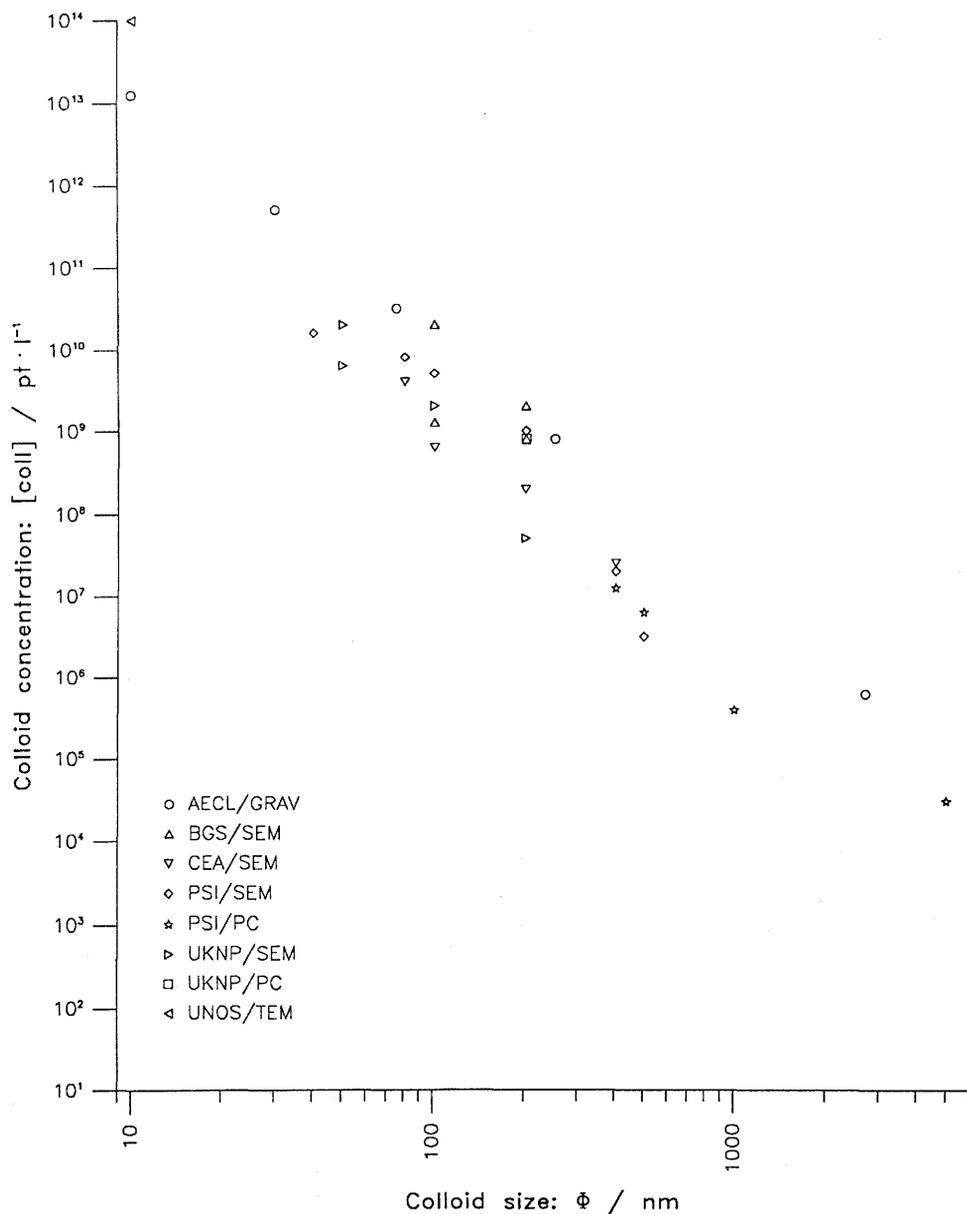


Figure 23: Intercomparison of particle/colloid concentration profiles for the groundwater.

it is easier to differentiate colloids from aggregates. The linear dependence of the logarithm of the colloid concentration as a function of the filtered volume and the fact that the slope decreases with increasing particle size show (Figure 21_a) that there is no contamination or artefact production during the sample preparation and transport/storage. A comparison of BGS and PSI counting results for the PSI1-5 samples is given in Figure 21_b. The difference between BGS and PSI are not significant (less than a factor 2, see table 18).

A comparison of CEA and PSI specific size distributions allows the detection of differences in the subsample preparation process. The only differences are the active area of the membrane and stirring. The first parameter is included in the filtration geometry and the difference in the colloid concentrations reported in Tables 6 and 7 is not due to surface area effects. In fact, comparing the specific size distributions (Figures 9 and 22), the increase of the small-size population in the CEA sample may be due to the fact that the stirring prevents aggregation.

The global intercomparison of cumulative particle counting is reported in Table 22 and Figure 23. The comparison of the gravimetry results with all microscopy and particle counting one is performed using formula [6.1]. The concentrations estimated by LPAS (at first about $6 \cdot 10^9$ pt.l⁻¹ after 450nm prefiltration, later $\approx 4 \cdot 10^{11}$ pt.l⁻¹ for $\varnothing_{(a)} = 100$ nm) and by SLS (about 10^{10} pt.l⁻¹) are not reported in this table because they were not determined as function of colloid size but were derived from assumption as to their size.

Table 22: Intercomparison of the cumulative particle/colloid concentration profiles, results for the original groundwater.

$\varnothing_{(m)}/nm$	AECL/GRAV	BGS/SEM	CEA/SEM	PSI/SEM/PC	UKNP/SEM/PC	UNOS/TEM	VTT/SEM
10	13.1					14.	
30	11.7						
40				10.2			11.0
50					10.3		
75	10.5						
80			9.6	9.9			
100		10.2-9.1	8.8	9.7	9.3		9.1
200		9.3-8.9	8.3	9.0	7.7/8.9		8.1
250	8.9						
400			7.4	7.3/7.1			
500				6.5/6.8			
1000				5.6			
2700	5.8						
5000				4.5			
7500	4.5						

Conditions: $\varnothing_{(m)}$ is the diameter of the smallest counted size, the concentrations are given in $\log([\text{coll}]/\text{pt.l}^{-1})$. Data selected are recommended by each characterisation as representative of the in-situ situation. AECL from Table 9 + conversion with [6.1], BGS from Table 5, CEA from Table 6, PSI from Table 7, UKNP from Table 8, VTT data from Figure 20.

The comparison of average size distribution indicates several important points. UKC DLS measurements indicate an average colloid diameter of about 4 to 6 μm . This diameter is larger than that derived by combining MF/SLS or UF/SEM or UF/GRAV. However, the results suggest that colloids may exist as fragile aggregates of much smaller particles. Indeed there may be a dynamic equilibrium between discrete particles and a fraction of larger associated structures, although there

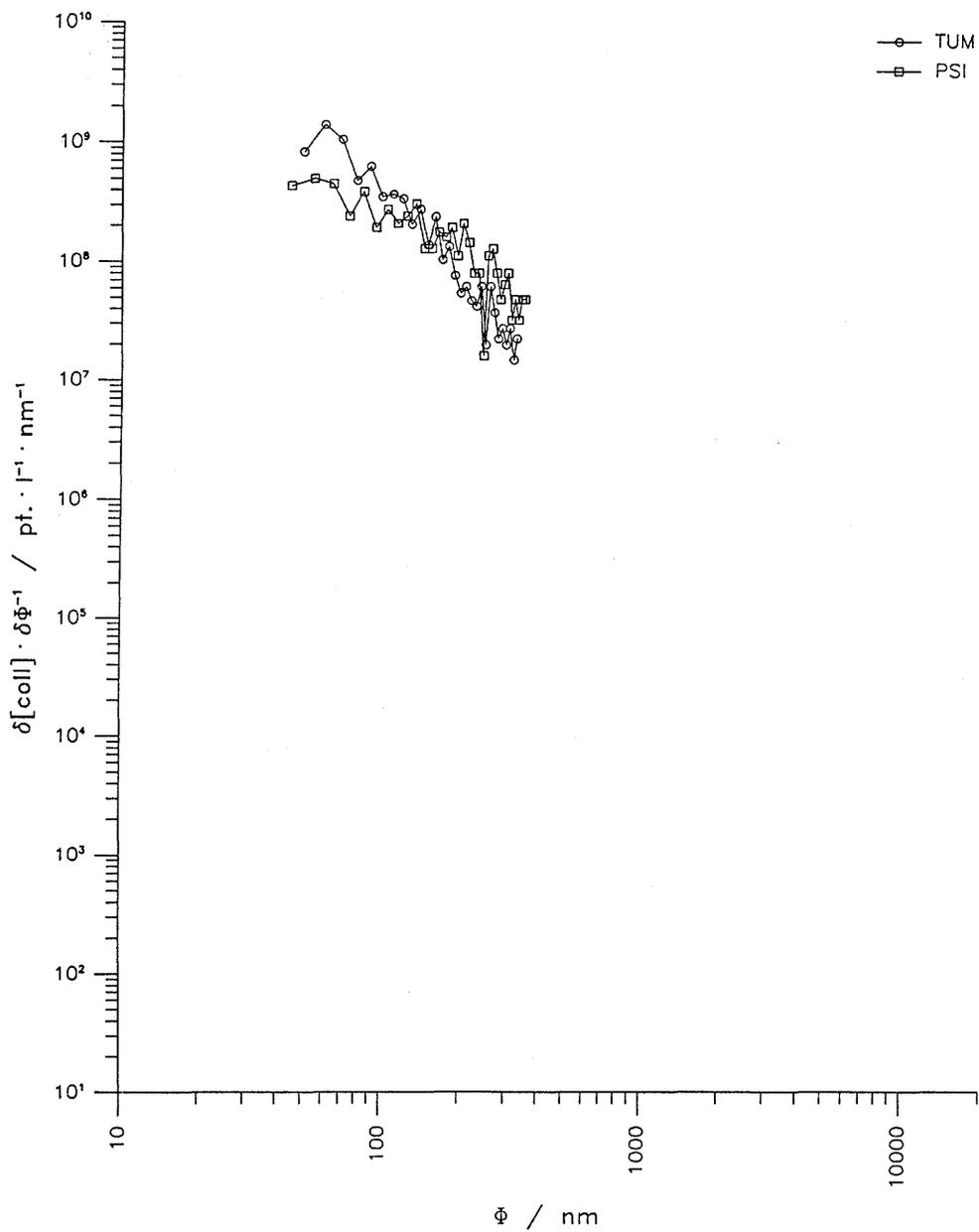


Figure 24: PSI2' comparison of PSI and TUM SEM counting.

is no direct evidence for this. The results have not been extrapolated to zero sampling time and thus the hydrodynamic radius obtained is an average weighted towards the larger particles. However, UKNP DLS results with an average size of 3 μm are comparable to the average size distribution derived from the in-situ GRAV measurements (see Table 9: 2.5 μm for the range 10-25,000 nm). Concentrate production by TDUF (or even by UF) may lead to particle/mass losses by adsorption of the colloid on the membrane or by agglomeration. This is observed by SLS (Table 12) as the concentration in the concentrate (30X) is not 30 times larger than in the unfiltered water. In addition, the first LPAS results reported above were obtained after a 450 nm prefiltration of the water sample. Here again, prefiltration may trap part of the colloid population.

Figure 24 presents the comparison of SEM counting (TUM and PSI) of the AECL concentrate sample filtered onto a flat membrane according to PSI methodology. A good agreement (within a factor of 2) was found for both size distributions. The data on the AECL processed groundwater sample are compared in Table 23 and reported in Figure 25. Comparing the results for particles and colloids from Tables 7 and 10 for the samples PSI1 and 5 (76 and 150 ml) and PSI2' (96 ml), one can conclude that if there is no aggregation of particles (about $3 \cdot 10^7 \text{ pt.l}^{-1}$), the aggregation of colloids (ranging from $8 \cdot 10^8$ to some $10^{10} \text{ pt.l}^{-1}$ according to sample preparation) takes place when the colloids are concentrated. In Figure 25, the dispersion is presumed to be due to artefact production by salt retention and calcite precipitation for the separation under anaerobic conditions (AECL/GRAV) or contamination of samples processed at Whiteshell (AECL) and the aggregation of colloid in the phase obtained under aerobic conditions by PC and UF/SEM.

Table 23: Intercomparison of the cumulative particle/colloid concentration profiles for groundwater samples affected by artefact production.
Samples: AECL concentrate after transfer to the CEA, PSI and TUM laboratories and groundwater characterisation by TDUF/GRAV in the AECL laboratory.

$\varnothing_{(m)}$	AECL/GRAV	TUM/SEM	PSI/SEM/PC	CEA/SEM
10	13.8			
30	12.3			
40		8.8-9.2	9.0	
50		9.14	9.01	
70				9.0
75	11.2			
80		8.88	8.89	
100		8.73	8.82	
200		8.01	8.42	
250	9.6			
400			6.8	
500			5.4	
1000			4.9	
2700	6.5			
5000			3.4	
7500	5.1			

Conditions: $\varnothing_{(m)}$ is given in nm and the concentrations are corrected back to those in the original water in $\log([\text{coll}]/\text{pt.l}^{-1})$. AECL data from Table 11 converted with formula [6.1], TUM and PSI/SEM data from Figure 24, PSI/PC from Figure 14 and CEA from section 5.3.1.

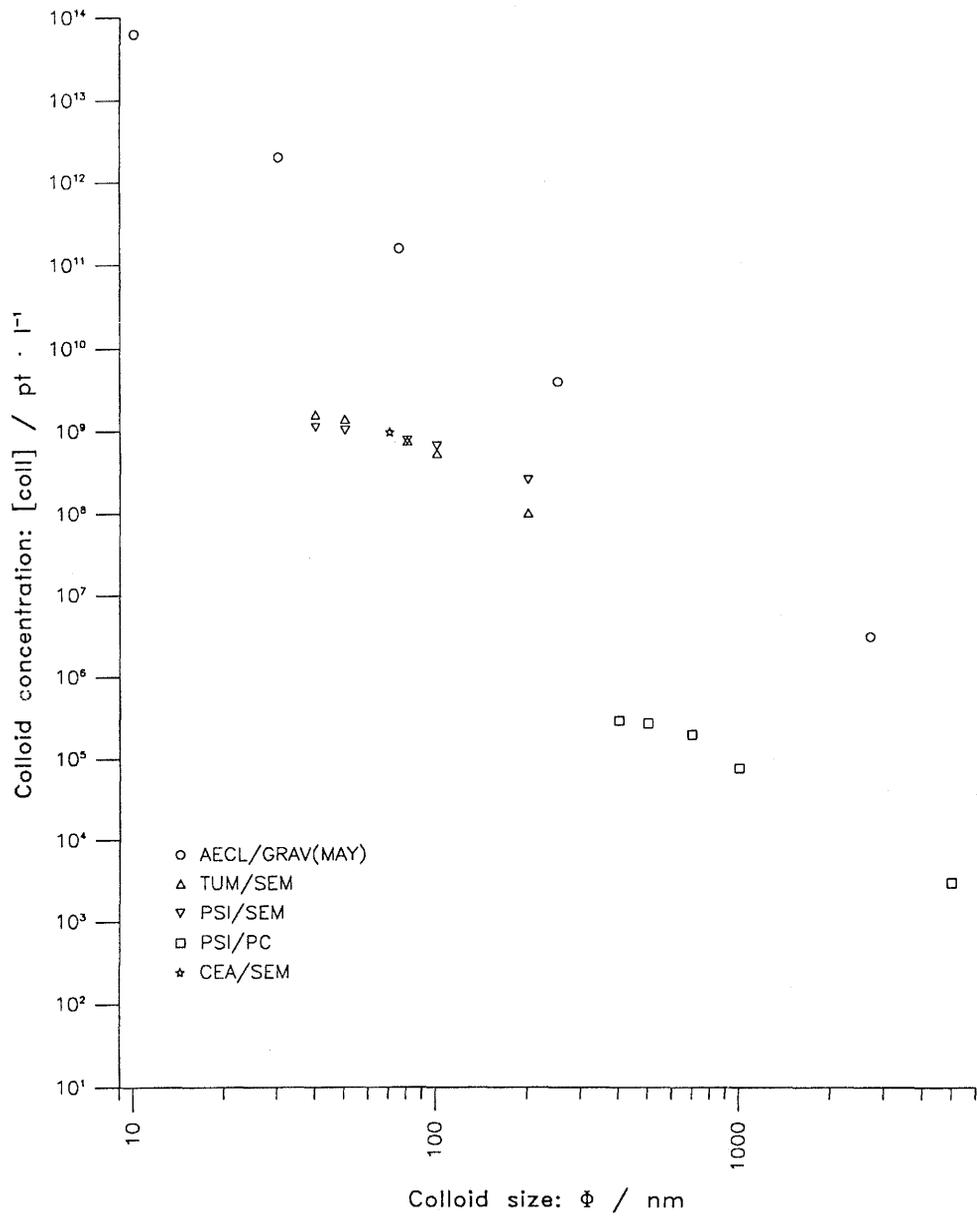


Figure 25: Intercomparison of particle/colloid concentration profiles for the groundwater processed with the AECL system.

The UKNP colloid concentrate is depleted in a fraction of the colloids. This is presumed to be due to the prefiltration which traps colloids (Tables 7 and 10 to be compared for sample PSI1 (76ml) and PSI1' (76ml)). This point is confirmed by [LON88]. UKNP found in their concentrate (38X) by combining UF and SEM that the colloid concentration ($\varnothing > 50$ nm) is $1.7 \cdot 10^{10}$, while for particles ($\varnothing > 300$ nm) the concentration was found to be $6.6 \cdot 10^8$ pt.l⁻¹. Techniques such as SLS, DLS, UC and TEM indicate the presence of colloids in the ultrafiltrate. This phenomenon is usual with organics which are able to pass through the membrane and aggregate in the filtrate. In addition, some membrane fragments or polymers leached from the filter may contaminate the filtrate which may be further perturbed by microbial growth. Contamination can also be enhanced during shipping, storage and analysis.

Since the agreement between the results obtained by SEM, PC, TEM and GRAV is excellent for the original samples (Table 22, Figure 23), the specific cumulative size distribution can be summarised by the following equations:

$$\log [\text{coll}] = 15.82 (\pm 0.36) - 3.17 (\pm 0.16) \log \varnothing \quad [6.5]$$

the normal size distribution is then:

$$\frac{\delta[\text{coll}]}{\delta\varnothing} = 10^{16.32} \cdot \varnothing^{-4.17} \quad (\text{absolute value}) \quad [6.6]$$

with \varnothing/nm ranging from 10 to 10,000 and $[\text{coll}]/\text{pt.l}^{-1}$ negligible for $\varnothing > 25,000$ nm. The exponent of equation [6.6] (Pareto's power law) is about 4 (constant mass concentration per size unit). This corresponds to an elimination mechanism including erosion of the "mylonite" according to a known fragmentation scheme [BUF88,LER79]. The total colloid/particle concentration consisting of SiO₂, clay, calcium silicate and organics is about 200 ppb. Concerning the characterisation of natural actinides as associated colloids, the only results reported for a comparison come from the fluorescence (LFS) and isotopic analysis of uranium (ICPMS, ANS). A comparison of the ratio of U fixed to the colloid to free U in groundwater is reported in Table 24 and ranges from 0.25 to about 0.01 for the various analyses and samples. The difficulty stems perhaps from the fact that the concentration level is so small ([U] about 50 ppt) that the contamination risks induce increases in data dispersion.

Table 24: Comparison of U concentrations and of the U association ratio for the Grimsel colloids and particles.

	AECL4*/AECL**	AECL1*/CEA**	UKNP2*/UKNP**	PSI*/PSI**
[U] _{coll} /ppt	7.8	2.-	0.53	<8.-
[U] _{tot.} /ppt	76.-	50-10	35.-	150-30
Ratio	0.11	0.25-0.04	0.01	<0.05-.. (ANS)

* sample ** characterisation group. Ratio = $[\text{U}]_{\text{coll}} \cdot \{[\text{U}]_{\text{tot.}} - [\text{U}]_{\text{coll}}\}^{-1}$

Finally, the CEC_(m) defined with the equation [6.3] is given by:

$$\text{CEC}_{(m)} = 2.79 \cdot 10^{-7} \cdot \varnothing^{-1.17} \quad [6.7]$$

with CEC/M, $\epsilon = 3$ nm², \varnothing/nm ranging from 10 to 10,000 nm. The CEC_(m) and CEC_(M), as calculated with [6.3] and [6.4], are respectively: 3 and 10² nM for the colloids (40-450nm) and 0.2 and 2 10² nM for particles (0.45-25 μm). Even with a superconcentrate (AECL3), the tests carried out in the laboratories with classic sorption on the surface of colloids/particles were below detection limit (10 nM corrected back to the original water). In view of this, it is estimated that the values for CEC_(M) derived above are probably too large.

7 CONCLUSIONS AND RECOMMENDATIONS

For an assessment of the impact of colloids on repository safety colloids have to be characterized and appropriate data for models collected. There is no "colloidograph" which allows on-line production of data such as size distribution, concentration and composition of the original colloid and associated colloid phases. All that can be done is to adapt an analytical system to produce some of the required data on the site or to transfer subsamples from the site to the laboratory and characterise them using various analytical techniques.

However, with this exercise, progress has been made in the understanding of colloid sampling and characterisation. For the Grimsel Colloid Exercise, the colloid phase was stabilised because of the high pH, both colloidal matter and the container (glass) being expected to be predominantly negatively charged. Because of the risk of altering the original sample by transport and storage, priority is to be given to sample preparation in-situ. In addition, some chemical analyses such as organic and inorganic carbon should be performed on site or shortly after sample collection. These precautions should improve the accuracy of data production. Calibration with standards which reflect the actual polydispersity and/or heterogeneity of the natural system is also essential.

For the Grimsel colloids, specific size distributions derived from sequential gravimetric tests, ultrafiltration followed by electron microscopic counting and single particle counting by light scattering are all comparable for the original samples. Interferences are noticed for the concentrated fluid samples and associated colloid evaluation has to be corrected using data obtained from multiprocessed samples (ultrafiltrate refractionated) to eliminate interferences such as salt retention. In addition, mention should be made of the difficulties involved in producing realistic and accurate results by LPAS and DLS for natural systems. Other non-separation techniques such as small angle neutron scattering and fluorescence are not yet applicable to natural polydispersed systems [YAN89].

Microfiltration and ultrafiltration remain reference techniques for determining size distribution on the basis of filtrate analysis or colloid sample preparation on the surface of the membrane. When combining scanning electron microscopy or gravimetry with both filtration techniques some assumptions have to be made including:

- total recovery of the colloids
- no reaction between the colloids and the membrane
- good colloid adherence to the membrane and no losses before weighing or counting
- for electron microscopy, the treatment must not alter the membrane or the colloids.

The smallest colloids may be enlarged by the SEM coating, while the TEM sees these colloids without preparation. For both techniques, focussing the electron beam on a single spot may cause significant "burn" damage to the exposed sample surface.

When combining prefiltration and flow-filtration, cross-flow prefiltration should not be used without studying the influence of prefiltration on the colloid content. With large specific area filters, trapping of colloids when filtering particles may occur. Later, when the prefilter is covered with a layer of particles, the prefiltration becomes a gelfiltration. Some authors claim that prefiltration is unsuitable [DAN82]. We suggest tangential flow prefiltration with an inert thin membrane.

Tangential flow ultrafiltration should not be performed with a single concentration factor. Fractionation work should be carried out with different enrichment factors and under various

pressure conditions. In addition, blank studies with filtrate or synthetic water must be done for interference detection. These precautions should allow improved detection of salt retention (reverse osmosis [BUF88]) and other interferences (inducing precipitation, clogging [MAZ88], etc) so that association ratios derived from these raw fractionation data can be corrected. Two possibilities for improving the quality of the concentrate are: working at equilibrium (e.g. dialysis) with low cut-off ($\varnothing < 10\text{nm}$) or working with tangential flow ultrafiltration and larger cut-off ($\varnothing > 10\text{nm}$). Some authors [SHO88] are already following the second procedure. Calculations on the basis of data not corrected from the blank lead to inaccurate or over-estimated association ratios.

The agreement (within an order of magnitude) between the results obtained by particle counting and transmission electron microscopy or by combining filtration and scanning electron microscopy or gravimetry is excellent for the original samples and the specific cumulative size distribution for the original samples is given by the following equation:

$$\log [\text{coll}] = 15.82 (\pm 0.36) - 3.17 (\pm 0.16) \log \varnothing$$

the normal size distribution is then:

$$\frac{\delta[\text{coll}]}{\delta\varnothing} = 10^{16.32} \cdot \varnothing^{-4.17} \quad *$$

with \varnothing/nm ranging from 10 to 10,000 and $[\text{coll}]/\text{pt.l}^{-1}$ negligible for $\varnothing > 25,000\text{ nm}$. The exponent of Pareto's power law is about 4 corresponding to an elimination mechanism that includes velocity gradients within the water mass [BUF88]. The colloid generation is probably due mainly to the erosion of the infill material of the granitic fissure according to the fragmentation scheme described in [LER79]. The total colloid/particle concentration is about 200 ppb. The colloidal phase consists of SiO_2 , illite/muscovite/biotite phases, calcium silicates (e.g. actinolite), organics and bacteria ($\approx 10^6\text{ bact.l}^{-1}$).

We are still a long way from truly understanding groundwater colloids, but progress has been made with respect to sampling and characterisation. There is no perfect method for colloid characterisation. Combinations of analytical techniques are therefore recommended. Problems for each method have been identified and some recommendations have made. We hope this work will prove useful for future sampling and characterisation studies.

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* In this report the absolute value is used in agreement with literature [BUF88].

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10 LIST OF ABBREVIATIONS

AAS	: atomic absorption spectrometry
AECL	: Atomic Energy of Canada Limited, Pinawa (C)
ANS	: alpha nuclear spectroscopy
BGS	: British Geological Survey, Keyworth (UK)
BRM	: Bureau of reference material (EC), Geel (B)
CEA-FAR	: Commissariat à l'Energie Atomique, Fontenay aux Roses
CEC	: cation exchange capacity
COC	: colloidal organic carbon
coll	: colloid
DIA	: dialysis
DLS	: dynamic light scattering
EC	: European Community
EDS	: Energy dispersive X-ray spectroscopy
GRAV	: gravimetry
GNS	: gamma nuclear spectroscopy
H	: height of water (in the PDUF system)
IC	: ion chromatography
ICP	: inductively coupled plasma atomic emission spectroscopy
ICPMS	: inductively coupled plasma mass spectroscopy
JRC	: Joint Research Centre (EC), Ispra (I)
KUL	: Katholieke Universiteit Leuven, Leuven (B)
LFS	: laser fluorospectrometry
LPAS	: laser-induced photoacoustic spectroscopy
ME	: microelectrophoresis
MF	: microfiltration
NA	: Instrumental neutron activation analysis
NBS	: National Bureau of Standards, Washington DC (USA).
part	: particle (> 450 nm)
PC	: particle counting
PDUF	: pulsed diaultrafiltration
PSI	: Paul Scherrer Institut, Villigen (CH)
ppb	: parts per billion
ppm	: parts per million
ppt	: parts per trillion
pt	: particle
SE	: specific electrode
SEM	: scanning electron microscopy
SLS	: static light scattering
TEM	: transmission electron microscopy
T	: temperature
TIC	: total inorganic carbon
TOC	: total organic carbon
TUM	: Technische Universitaet Muenchen, Garching (D)
UC	: ultracentrifugation
UF	: ultrafiltration
UKC	: Harwell Laboratories, Chemistry Division, Harwell (UK)
UKNP	: Harwell Laboratories, Nuclear Physic Division, Harwell (UK)
UNAN	: University of Nantes, Nantes (F)
UNOS	: Agricultural University of Norway, Aas (N)
UVS	: Ultraviolet spectroscopy
vpm	: volume per million
VTT	: Technical Research Centre of Finland, Espoo (SF)
XRD	: X-ray diffraction

\emptyset : particle/colloid diameter
 $\emptyset_{(a)}$: average diameter
 $\emptyset_{(m)}$: minimum diameter
 $\emptyset_{(M)}$: maximum diameter
 η : water viscosity
 ρ : average density of colloids
 ω : angular velocity of UF rotor in radian.s^{-1}
 ϵ : site density
 λ : wave length

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