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Characterization of humic substances from deep groundwaters in granitic bedrock in Sweden

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CHARACTERIZATION OF HUMIC SUBSTANCES FROM DEEP
GROUNDWATERS IN GRANITIC BEDROCK IN SWEDEN

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**CHARACTERIZATION OF HUMIC SUBSTANCES FROM DEEP GROUNDWATERS IN
GRANITIC BEDROCK IN SWEDEN**

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ABSTRACT

Humic substances were isolated from deep groundwaters sampled at depths between 100 and 800 m at Finnsjön, Fjällveden, Forsmark, Gideå, Lansjärv, Stripa and Äspö. The humic fraction, which largely consisted of fulvic acid in all the samples, was characterized with respect to elemental composition, molecular weight, acid capacity (COOH and OH) as well as age (^{14}C). The differences in composition and capacity between old (1270-9675 y) and fresh (reference fulvic acid from surface water, Bersbo) were minor.

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INTRODUCTION

Dissolved organic carbon (DOC) of natural origin is found in surface waters and groundwaters as well as in precipitation. A major part of the DOC in surface water is composed of humic substances, while in groundwaters, especially at great depth (long residence times), the humic substances could be the minor part. The concentration of the aquatic humic substances varies remarkably in different types of water, from ca 100 mg/l in a bog water to ca 1 ug/l in a deep groundwater.

Humics comprise a large heterogenic group of organic substances derived from microbially decomposed biologic materials such as plant tissue. The water soluble humic substances are largely composed of aliphatic and aromatic hydrocarbons containing acidic functional groups (e.g. carboxyl and hydroxyl groups) and have molecular weights ranging from a few hundred to above 10000 Daltons /Thurman, 1986/, thus making them behave as polyelectrolytes. They have a high complexing capacity, due to the presence of acidic groups with pK_a -values within the environmental pH-range, and they form strong complexes particularly with highly-charged cationic metal species.

Humic substances influence several processes in surface water and groundwaters. Some of them are:

- The chemical speciation of particularly trace metals is affected, and thereby interactions with solid surfaces, distribution, mobility and transport properties etc.
- The bioavailability, and thereby the toxicity, of trace elements is affected
- The acid-base properties influence pH of the water and have a buffering effect
- The oxidation state of cationic redox sensitive elements is affected, the humics being fairly strong reducing agents (e.g. stabilizing the lower oxidation states for Fe, Tc, Np, Pu etc.)

- The ion exchange properties affect the balance between major cations
- Precipitation of a solid or colloid phases is related to the presence of particularly high-molecular weight humics (also dependent of pH and concentrations of highly charged metal species)

The strong metal complexing capacity of the humic substances makes it important to study their occurrence and distribution in the vicinity of nuclear waste and mine waste deposits. The presence of humic substances has a great influence on the extent to which leached radionuclides and trace metals will be spread from the deposits by ground water or surface water.

In this report the isolation and characterization of seven fulvic acids (a fraction of the humic substances) from deep groundwaters are described. Their properties are compared with a surface water fulvic acid prepared by the same procedure.

2 SAMPLING OF HUMIC SUBSTANCES

2.1 DESCRIPTION OF THE SAMPLING SITES

Groundwaters from various locations in Sweden (Finnsjön, Fjällveden, Forsmark, Gideå, Lansjärv, Stripa and Äspö, see Figure 2-1) have been sampled and chemically analyzed as a part of the geological program within the Swedish nuclear waste project.

Humic substances, mainly the fulvic acid fraction, have been recovered from these sites and have been characterized according to the scheme described in section 2.3.2. For comparison the characterization of a surface water fulvic acid collected at Bersbo (Figure 2-1) is included in this report.

The sampling sites, all of them in granitic bedrock, are thoroughly investigated and described in other reports /Axelsen and Wikberg, 1982; Allard et al., 1983; Laurent, 1983a; Laurent, 1983b; Laurent, 1985; Nordstrom, 1985; Smellie et al, 1985; Puigdomenech and Nordstrom, 1987; Smellie et al, 1987; Wikberg et al, 1987; Laaksoharjo, 1988/.

2.2 CHEMICAL PROPERTIES OF THE GROUNDWATERS

The chemical composition of the various groundwaters was determined within the geological and hydrological program of the Swedish nuclear waste project. The analyses are summarized in Table 2-1.

The pH values vary from 7.5 to 9.7 for the groundwaters. Four of the waters, Fj, G, L, and S, have a low content of dissolved components and can be considered as typical deep groundwaters from a granitic bedrock environment, while Fi, Fo, and Å can be considered as saline waters.

2.3 ISOLATION AND CHARACTERIZATION OF HUMIC SUBSTANCES

2.3.1 **The isolation procedure**

The humic substances were recovered by adsorption to a weak anion exchanger, DEAE-cellulose. The technique for isolation and purification of the humic material is based on methods described in the

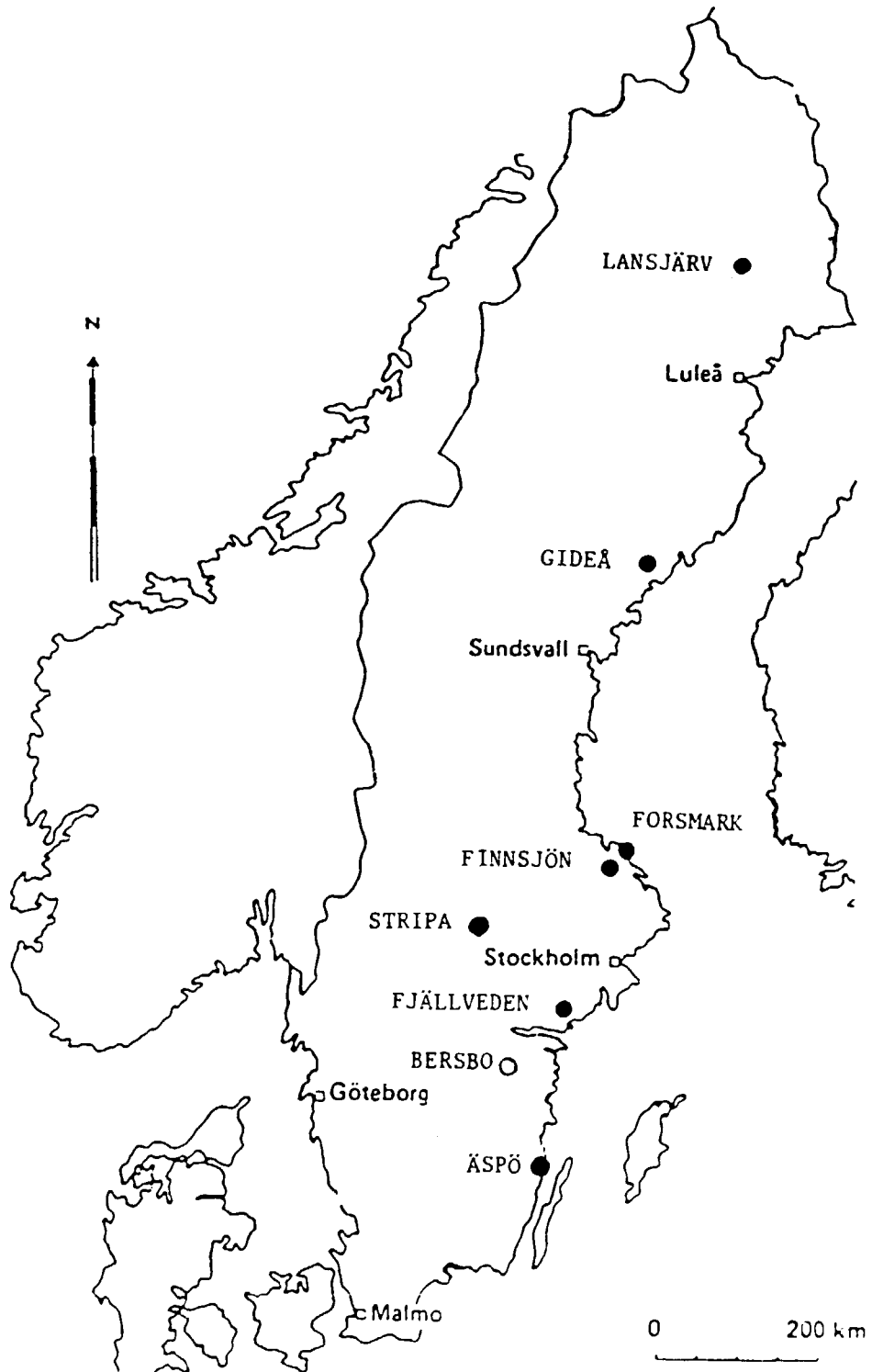


Fig. 2-1 Groundwater sampling locations

Table 2-1 Chemical properties of the groundwaters

| Location | F1 | F1 | Fo | G | L | S | A | B |
|--------------------------------------|-------|------|------|-------|------|----------|-------|------|
| Depth (m) | 232 | 409 | <100 | 157 | 139 | 800 | 530 | 0 |
| Age (y)* | 8090 | 4235 | | 6450 | nd | 25000 | nd | nd |
| Tritium (TU) | <3 | 19 | | <3 | | <1 | | |
| pH | 7.7 | 7.5 | 7.2 | 8.8 | 7.6 | 9.7 | 8.0 | 5.2 |
| Cond. (mS/m) | 531 | 30 | 1240 | 27.5 | 9.7 | 0.4 | 1880 | 10.5 |
| HCO ₃ ⁻ (mg/l) | 260 | 170 | 66 | 161 | 55 | 15 | 11.1 | 5.5 |
| SO ₄ ²⁻ " | 140 | 0.2 | 180 | 0.8 | 1.6 | 4 | 545 | 36 |
| Cl ⁻ " | 1500 | 7 | 3800 | 4.4 | 0.8 | 240 | 6398 | 7.2 |
| Na ⁺ " | 650 | 32 | 1400 | 49 | 5.1 | 93 | 2130 | 5.8 |
| K ⁺ " | 8.7 | 2.5 | 12 | 2.2 | 0.9 | 0.23 | 8.1 | 1.8 |
| Mg ²⁺ " | 40 | 0.4 | 140 | 2.6 | 2.9 | 0.08 | 42 | 8.6 |
| Ca ²⁺ " | 320 | 21 | 970 | 10 | 10.4 | 31 | 1890 | 8.3 |
| Fe (tot) " | 0.87 | 6.5 | 0.93 | 0.13 | 0.8 | 0.004 | 0.290 | 3.1 |
| SiO ₂ | 16 | 13 | | 22 | | | | |
| Ref. | [1,2] | [3] | [4] | [5,6] | [7] | [8,9,10] | [7] | [11] |

*From the ¹⁴C-content of the CO₂-fraction, after correction for the ¹³C-content.

References: [1] Smellie et al., 1985; [2] Smellie et al., 1987; [3] Laurent, 1983a; [4] Wikberg, 1985; [5] Smellie et al., 1985; [6] Laurent, 1983b; [7] Wikberg, 1989; [8] Lindström, 1989; Fritz et al., 1989; [10] Moser et al., 1989; [11] Karlsson, 1987

literature /Thurman and Malcolm, 1981; Paxeus, 1985/ and further developed /Allard et al., 1990/. The DEAE-cellulose has its optimum adsorption for humic substances at the pH range 5-8 /Miles et al., 1983/ thus making it possible to isolate the humic material at the natural pH of the water.

In the recovery of humic substances from the deep groundwaters a filter tube filled with DEAE-cellulose was connected directly to the outlet of water that was pumped up from the borehole. The pH of the water collected from Stripa was too high (9.7) to allow the humic substances to be adsorbed onto the resin. This water was collected in a 100-l barrel and acidified to pH 6 with HCl before adsorption to DEAE-cellulose by a batch procedure.

The humic substances were desorbed from the resin and the eluate was acidified to pH 1 in order to separate humic acid (insoluble at pH 1) from fulvic acid (soluble in the whole pH range). As humic substances from groundwater mainly consist of fulvic acid, only this fraction was purified and freeze-dried.

In the purification step the low molecular organic material as well as chlorides and cations were removed. Because of the extremely small amounts of humic materials recovered from Forsmark and Äspö it has not been possible to purify these two samples.

The fulvic acid from Fjällveden was recovered in a slightly different way /Paxeus, 1985/. It was isolated on DEAE-cellulose as the other six humic substances, but the purification step was performed by precipitation in organic solvents.

The Bersbo fulvic acid was isolated on DEAE-cellulose by a batch procedure, followed by purification and freeze-drying.

The amounts of fulvic acids recovered from the deep groundwaters are listed in Appendix 1.

2.3.2 **The characterization procedure**

The characterization scheme for the fulvic acids described in this section has previously been developed /Allard et al., 1990/. A complete characterization was performed for the samples from Finnsjön, Fjällveden, Gideå and Stripa. Just a few analyses could be made on samples from Forsmark, Lansjärv and Äspö.

2.3.2.1 Elemental analysis

Major elements (C, H, O, N, S) were determined (by Mikro Kemi AB, Uppsala, Sweden).

2.3.2.2 Molecular weight

Molecular weight (M_n and M_w) was determined with GPC-technique performed on a HPLC-equipment consisting of a Waters 510 pump, a column TSK G2000SW and a Waters 481 UV-detector (254 nm). The mobile phase was a 50 mM phosphate buffer at pH 6.8, with a flow rate of 0.5 ml/min. As reference substances, polystyrene sulphonates of known molecular weights were used /Becher et al., 1985/.

2.3.2.3 Acid-base properties

Acid-base properties were determined by potentiometric titration in aqueous and non-aqueous media. The acid-base titrations of the fulvic acids in aqueous solution were performed at three different ionic strengths (0.001 M, 0.010 M and 0.100 M NaClO₄) /Ephraim et al., 1989/.

2.3.2.4 Age

The age of the fulvic acid was determined by measurements of ^{14}C (by The Svedberg Laboratory, Uppsala, Sweden).

DISCUSSION

3.1 PROPERTIES OF THE HUMIC SUBSTANCES

The results of the characterization of the fulvic acids recovered from the waters described above are shown in Table 2-2.

Table 2-2 Properties of the fulvic acids

| Location | F1 | Fj | Fo | G | L | S | A | B |
|--------------------------------|------|------|------|------|------|------|------|------|
| Depth (m) | 232 | 409 | <100 | 157 | 139 | 800 | 530 | 0 |
| Age (y) ^a | 4610 | 1270 | nd | 5250 | 9675 | | nd | nd |
| Elemental anal.: | | | | | | | | |
| C (%) | 53.0 | 50.8 | nd | 53.7 | 52.9 | 39 | nd | 52.5 |
| H (%) | 3.8 | 3.9 | nd | 4.4 | 4.8 | 4 | nd | 3.6 |
| N (%) | 0.9 | 1.7 | nd | 0.5 | 1.1 | 1 | nd | 1.1 |
| O (%) | 36.2 | 39.7 | nd | 37.5 | 36.5 | 31 | nd | 38.8 |
| S (%) | 1.1 | 0.8 | nd | 0.5 | 0.6 | 1 | nd | 1.0 |
| Ash (%) | 5.0 | 3.1 | nd | 3.4 | 4.3 | 24? | nd | 3.0 |
| M _n | 1750 | 1250 | | 1150 | 710 | 930 | 950 | 1750 |
| M _w | 2650 | 1700 | | 1600 | 820 | 1090 | 1120 | 2650 |
| M _w /M _n | 1.51 | 1.36 | | 1.39 | 1.15 | 1.17 | 1.18 | 1.51 |
| Aq. acid cap. (meq/g) | | | | | | | | |
| | 4.98 | 5.14 | nd | 5.42 | nd | 3.72 | nd | 4.65 |
| Non-aq. acid cap. (meq/g) | | | | | | | | |
| COOH | 4.16 | 5.56 | nd | 5.33 | nd | | nd | 4.78 |
| OH | 0.83 | 2.53 | nd | 1.05 | nd | | nd | 1.35 |
| Total | 4.99 | 8.09 | nd | 6.38 | nd | | nd | 6.13 |

^aFrom the ¹⁴C-content of the fulvic acid fraction of the DOC.

Molecular weights were determined both as number average molecular weight, M_n, and as weight average molecular weight, M_w. The ratio M_w/M_n expresses the molecular weight distribution of the samples. The closer to unity, the more homogenous the sample, which indicates a more decomposed material.

Although the composition of fulvic acids from entirely different locations appears to be similar, a detailed comparison and discussion of differences should be made with caution.

3.1.1 Elemental analysis

Fulvic acids in groundwaters, as well as in surface waters, are decomposed by microbial activity and

possibly by chemical processes generating a change in elemental composition. The oxygen and nitrogen content is generally decreasing while the carbon content is increasing /Thurman, 1985/.

All the present fulvic acids were quite similar in elemental composition. In the older fulvic acids, i.e. >2000 years, there was indeed a decrease in the oxygen content and a slight increase in the carbon content.

3.1.2 **Molecular weight**

A comparison between the surface water fulvic acid, B, and the groundwater fulvic acids indicates, from the decrease in molecular weight, a progressing decomposition of humic substances in groundwater. However, the Finnsjön fulvic acid, recovered from a saline water, was an exception having the same molecular weight as the surface water fulvic acid.

There was a variation in the ratio M_w/M_n between the different fulvic acids. The value for L, S and Å was rather close to unity, which coincided for L and S with their higher ^{14}C -age compared to other dated fulvic acids (^{14}C in Å was not measured). The low value of the ratio could be a result of the long residence time for these fulvic acids. The other (younger) groundwater fulvic acids had a molecular weight distribution that was quite similar to that of the surface water fulvic acid. This suggests that decomposition of fulvic acids in groundwater is a very slow process compared to the decomposition rate in soils /Thurman, 1985/.

3.1.3 **Acid-base properties**

The acid-base properties of the various fulvic acids have been described with the following conceptualization as the basis: Humic substances are an assemblage of relatively small hydrophobic moieties which are slightly different but composed of four to five predominantly separate acidic sites with each site characterized by a distribution of acid strengths which be averaged.

For two of the fulvic acid samples, i.e. Fi /Ephraim, et al. 1988/ and B /Ephraim et al., 1989/, the effects of ionic strength and the heterogeneity on their potentiometric properties have been identified and quantitatively described employing an already existent approach /Ephraim et al., 1986/. Insight into the acidic spectrum

existent in the various fulvic acids are obtained by a comparison of the total acidities determined in aqueous and non-aqueous media. For example different amounts of an -OH moiety are detected in the non-aqueous titrations (for Fi 17%, Fj 31%, G 16%, B 22%).

The ability to quantify ionic strength effects and the designation of predominant acidic sites will facilitate the incorporation of the role of humic substances into speciation programs, eg. Minigl, PHREEQUE etc.

3.1.4 Age

Average residence times for groundwater in an aquifer is usually determined by analysis of the ^{14}C -content of the inorganic carbon fraction, i.e. the carbonates. The ages could be incorrectly estimated because of uncontrollable processes in the subsurface: Chemical and isotopic exchange with CO_2 ; sensitivity of the carbonate equilibrium to changes in temperature and chemical conditions; exchange reactions between dissolved carbonate and solid carbonate minerals; subsurface production.

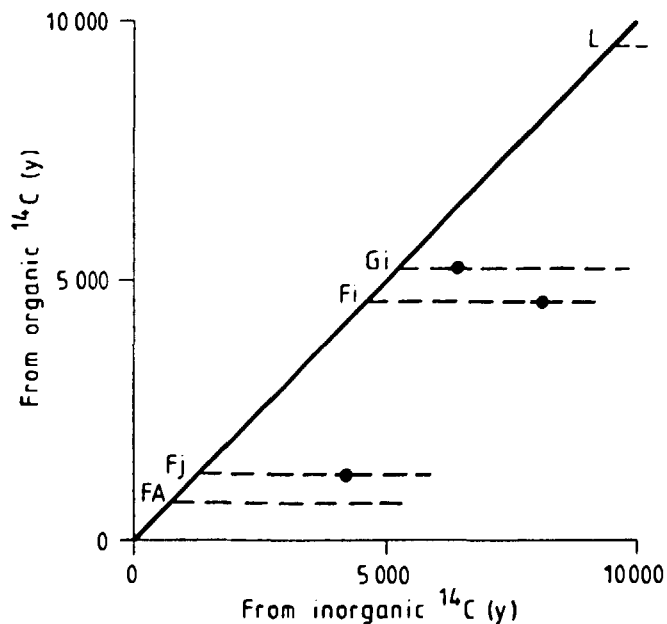


Fig. 3-1 Correlation of the ages from organic ^{14}C and inorganic ^{14}C for the various fulvic acids.

The low organic content of the groundwaters requires a technique analysing very small amounts of ^{14}C . The use of a tandem accelerator mass

spectrometer makes it possible to determine the ^{14}C -content on samples of only a few milligrams.

The ages measured from analysis of the ^{14}C -content of the fulvic acids vary from 1000 to 10000(?) years. In Figure 3-1 the correlation between the inorganic ^{14}C -age (originating from the carbonate) and the organic ^{14}C -age (originating from the fulvic acid) is illustrated for some of the samples.

The inorganic ^{14}C -age indicates an older water than the organic ^{14}C -age. The dissolved inorganic carbon (carbonate) content would be modified by several chemical reactions, which would alter the ^{14}C -content and hence influence the age determination, generally towards a higher age. Side reactions that would significantly affect the ^{14}C -content of the fulvic acid are presently not known. The recovering technique used does not concentrate hydrocarbons, which means that there would not be any significant influence on the ^{14}C -content from old hydrocarbons in the aquifer. Thus, the use of fulvic acid as a ^{14}C -source in age determinations seems to be preferable.

3.2

CHEMICAL DEGRADATION

A comparison of chemical data (elemental composition, molecular weight, capacity; cf. Table 2-2) shows that there are only minor differences between the reference fulvic acid from a surface water and the old fulvic acids from deep groundwaters with the exception of the Stripa sample, which has a high ash content of unknown composition.

Possibly, the M_w/M_n -ratio is closer to unity for the old samples, but truly significant differences in molecular weight can not be distinguished. However, the fulvic acids with the lowest molecular weights are among the oldest.

The OH/COOH-ratio is decreasing somewhat with age; the Fjällveden sample is an exception that can be due to the fact that the corresponding water is a mixture of old and fairly recent waters.

Except for Stripa, there are no obvious effects of the water quality on the composition of the corresponding humic materials (c.f. high-pH water from Gideå; high salinity in the water from Finnsjön). However, data are not available for the

humics from the old and saline waters from Forsmark and Äspö, but the total concentrations of humic substances are quite low in both these waters (< 0.01 mg/l).

CONCLUSIONS

It can be concluded that

- Fulvic acids dominate in the humics from deep groundwaters
- The fulvic fraction is very stable; differences in composition, molecular weight and acid capacity between old and fresh materials are minor
- Possibly, molecular weight and the M_w/M_n -ratio decrease with age, as well as the OH/COOH-ratio
- Total concentrations are low in old waters, possibly also in saline waters (which are generally old)

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APPENDIX 1

FULVIC ACIDS RECOVERED FROM DEEP GROUNDWATERS

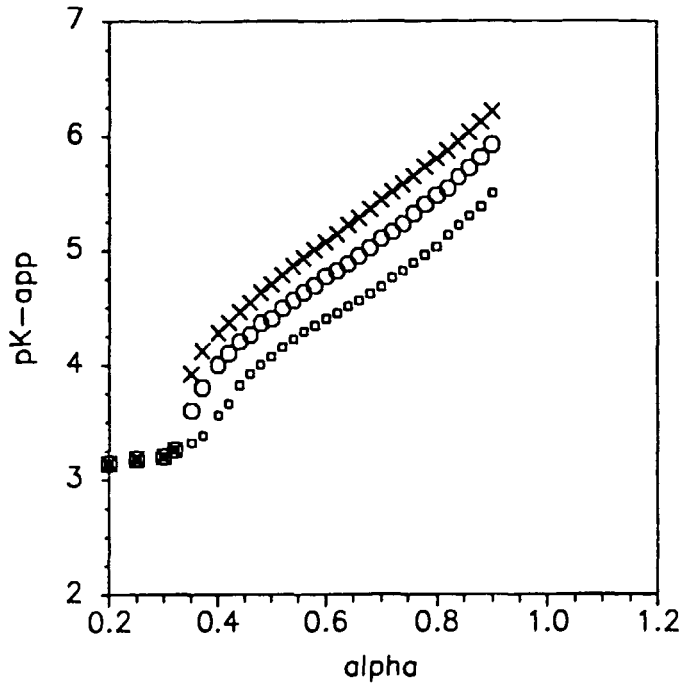
| | |
|-------------------------|--------|
| Finnsjön | 650 mg |
| Fjällveden ^a | 300 mg |
| Forsmark ^b | 10 mg |
| Gideå | 220 mg |
| Lansjärv | 40 mg |
| Stripa | 94 mg |
| Äspö ^{b,c} | <10 mg |

^a Recovered by Paxeus /1985/, 300 mg available at Dept. of Water and Environmental Studies, Linköping

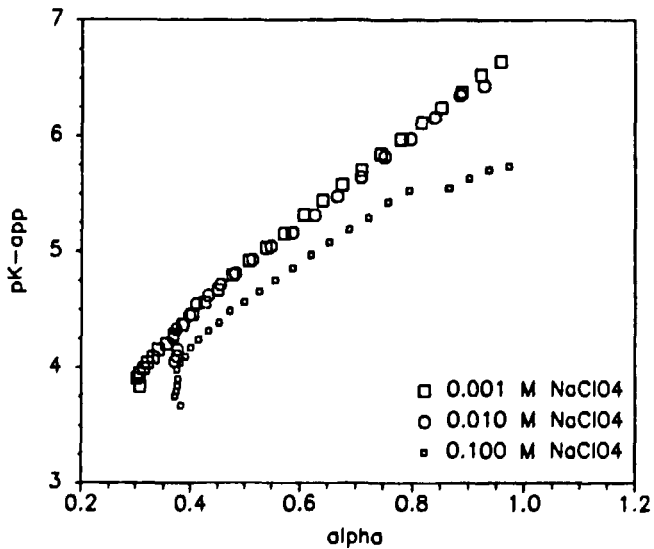
^b Not purified because of the small amount

^c Recovery was performed at five occasions; each time <10 mg was collected

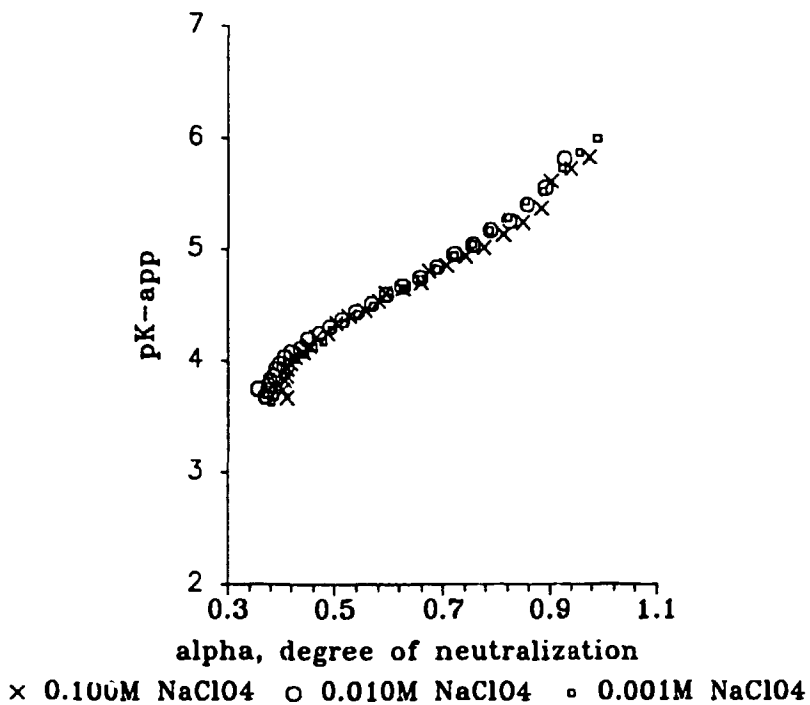
APPENDIX 2

Potentiometric titrations of fulvic acids**Potentiometric Titration of Bersbo FA
As A Function of Ionic Strength**

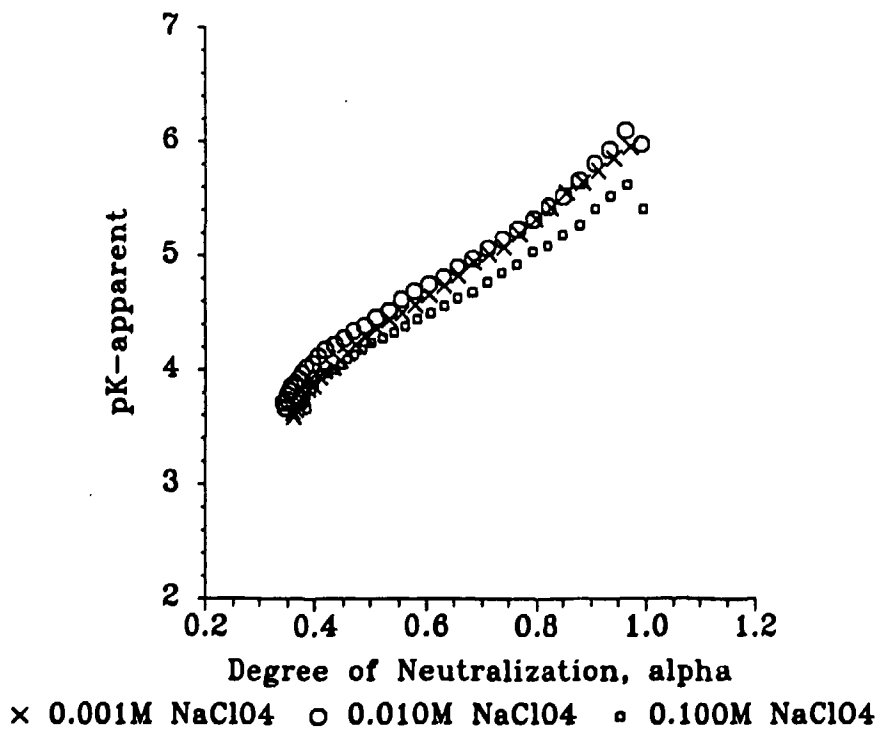
□ 0.100 M NaClO₄ o 0.010 M NaClO₄ x 0.001 M NaClO₄

**Potentiometric Titrations of Finsjön FA
As a Function of ionic Strength**

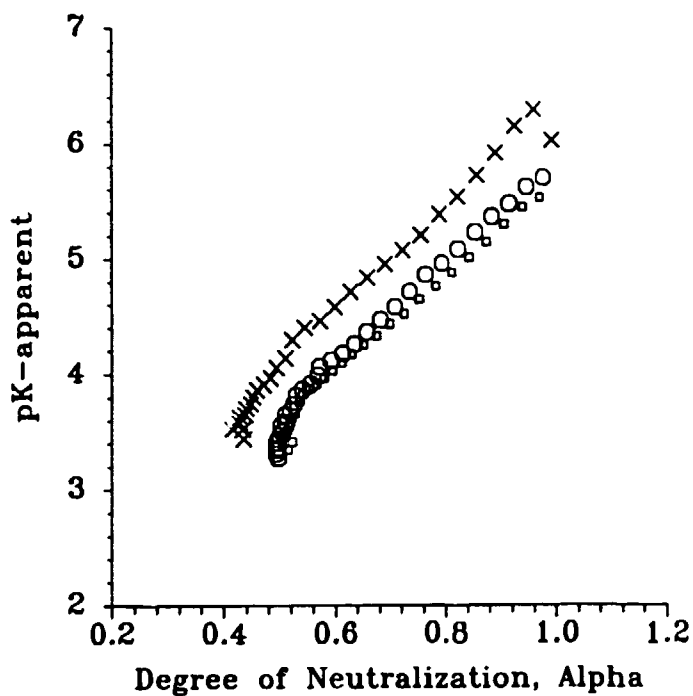
Potentiometric Titration of Vadstena FA



Potentiometric Titrations of Gidea FA
As A Function of Ionic Strength

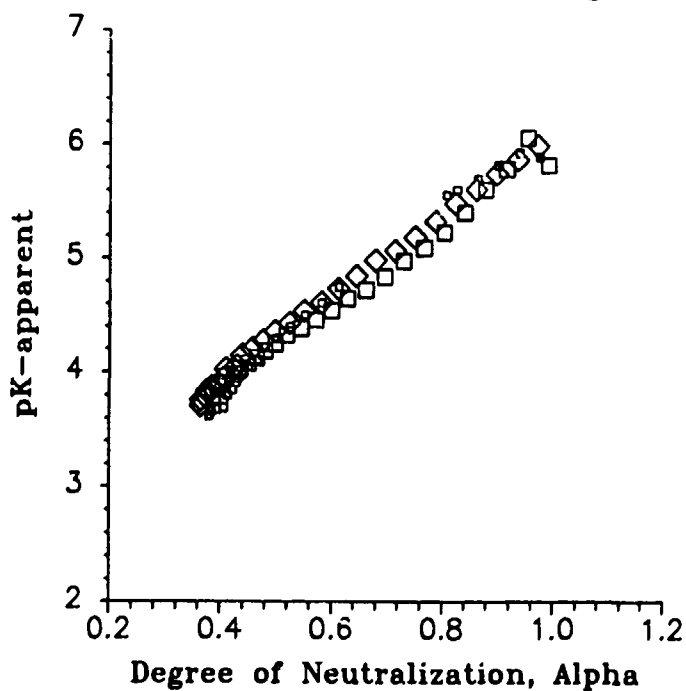


Potentiometric Titrations of Tiveden FA
As A Function Of Ionic Strength

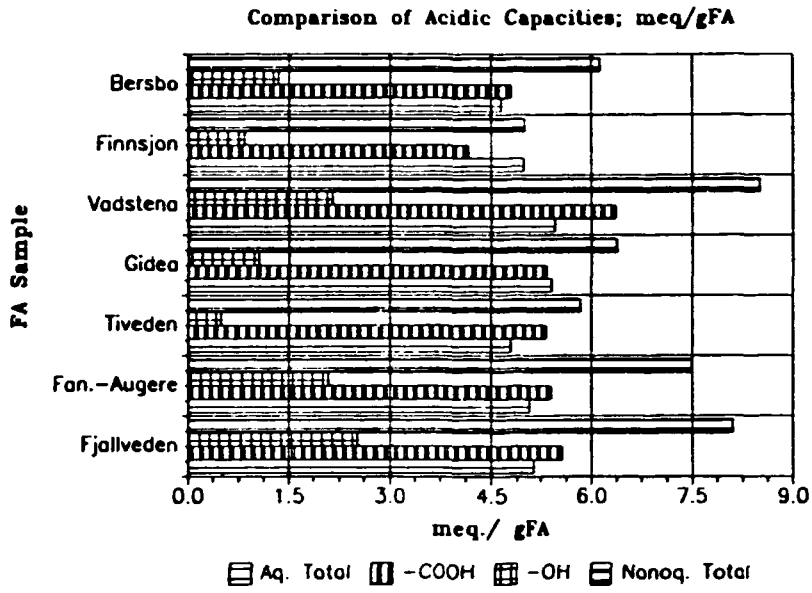


× 0.001M NaClO4 o 0.010M NaClO4 ◻ 0.100M NaClO4

Potentiometric Titrations of Fjällveden
FA As A Function of Ionic Strength



◻ 0.100M NaClO4 ◇ 0.010M NaClO4 o 0.001M NaClO4



List of SKB reports

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Summaries. Stockholm, May 1979.

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TR 79-28

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FARF31 -

A far field radionuclide migration code for use with the PROPER package

Sven Norman¹, Nils Kjellbert²

¹ Starprog AB

² SKB AB

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Source terms, isolation and radiological consequences of carbon-14 waste in the Swedish SFR repository

Rolf Hesbøl, Ignasi Puigdomenech, Sverker Evans Studsvik Nuclear

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Statistical estimation and stochastic simulation using PROPER

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² SKB AB

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Examination of the surface deposit on an irradiated PWR fuel specimen subjected to corrosion in deionized water

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University of Gothenburg, Department of General and Marine Microbiology, Gothenburg
January 1990

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Transport of actinides and Tc through a bentonite backfill containing small quantities of iron, copper or minerals in inert atmosphere

Yngve Albinsson, Birgit Sätmark, Ingemar Engkvist, W. Johansson
Department of Nuclear Chemistry, Chalmers University of Technology, Gothenburg
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Examination of reaction products on the surface of UO_2 fuel exposed to reactor coolant water during power operation

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Studsvik Nuclear
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Radiolytically induced oxidative dissolution of spent nuclear fuel

Lars Werme¹, Patrik Sellin¹, Roy Forsyth²
¹ Swedish Nuclear Fuel and waste Management Co (SKB)
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TR 90-09

Individual radiation doses from unit releases of long lived radionuclides

Ulla Bergström, Sture Nordlinder
Studsvik Nuclear
April 1990

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Outline of regional geology, mineralogy and geochemistry, Poços de Caldas, Minas Gerais, Brazil

H D Schorscher¹, M E Shea²
¹ University of Sao Paulo
² Battelle, Chicago
December 1990

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Mineralogy, petrology and geochemistry of the Poços de Caldas analogue study sites, Minas Gerais, Brazil.

I: Osamu Utsumi uranium mine
N Waber¹, H D Schorscher², A B MacKenzie³, T Peters¹
¹ University of Bern
² University of Sao Paulo
³ Scottish Universities Research & Reactor Centre (SURRC), Glasgow
December 1990

TR 90-12

Mineralogy, petrology and geochemistry of the Poços de Caldas analogue study sites, Minas Gerais, Brazil.

II: Morro do Ferro
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University of Bern
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Isotopic geochemical characterisation of selected nepheline syenites and phonolites from the Poços de Caldas alkaline complex, Minas Gerais, Brazil

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Battelle, Chicago
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Geomorphological and hydrogeological features of the Poços de Caldas caldera, and the Osamu Utsumi mine and Morro do Ferro analogue study sites, Brazil

D C Holmes¹, A E Pitty², R Noy¹
¹ British Geological Survey, Keyworth
² INTERRA/ECL, Leicestershire, UK
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Chemical and isotopic composition of groundwaters and their seasonal variability at the Osamu Utsumi and Morro do Ferro analogue study sites, Poços de Caldas, Brazil

D K Nordstrom¹, J A T Smellie², M Wolf³
¹ US Geological Survey, Menlo Park
² Conterra AB, Uppsala
³ Gesellschaft für Strahlen- und Umweltforschung (GSF), Munich
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TR 90-16

Natural radionuclide and stable element studies of rock samples from the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil

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Natural series nuclide and rare earth element geochemistry of waters from the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil

N Miekeley¹, O Coutinho de Jesus¹,
C-L Porto da Silveira¹, P Linsalata², J N Andrews³,
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Chemical and physical characterisation of suspended particles and colloids in waters from the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil

N Miekeley¹, O Coutinho de Jesus¹,
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Microbiological analysis at the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil

J West¹, A Vialta², I G McKinley³

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Testing of geochemical models in the Poços de Caldas analogue study

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J Cross¹, A Haworth¹, P C Lichtner²,
A B MacKenzie³, L Moreno⁴, I Neretnieks⁴,
D K Nordstrom⁵, D Read⁶, L Romero⁴,
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Near-field high temperature transport: Evidence from the genesis of the Osamu Utsumi uranium mine analogue site, Poços de Caldas, Brazil

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Geochemical modelling of water-rock interactions at the Osamu Utsumi mine and Morro do Ferro analogue sites, Poços de Caldas, Brazil

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The Poços de Caldas Project: Summary and implications for radioactive waste management

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**Kinetics of UO₂(s) dissolution reducing conditions:
numerical modelling**

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The effect from the number of cells, pH and lanthanide concentration on the sorption of promethium on gramnegative bacterium (Shewanella Putrefaciens)

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Isolation and characterization of humics from natural waters

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Complex forming properties of natural organic acids.

Part 2. Complexes with iron and calcium

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