

RAPID CHEMICAL PROCEDURES FOR RADIOANALYTICAL WASTE CONTROL (LAW AND MAW)

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ABSTRACT

Complete quality checking of radioactive waste packages requires destructive and non-destructive test methods. Available and suitable techniques for these purposes must be identified or modified according to the analytical task. In this contribution the rapid dissolution of low level cemented waste samples using a laboratory microwave oven is reported. Under relevant conditions inactive powdered cement samples are dissolved within 20 minutes leading to clear and stable solutions. In case of complex mixtures of radionuclides, separation of the elements is achieved with High Performance Liquid Chromatography (HPLC). The single elemental fractions are collected separately so that they can be measured free from interferences. Separation of Fe, U, Co, Ni, Mn requires only 25 min.

INTRODUCTION

Measurement and identification of the radionuclide inventory of radioactive waste is one of the most important criterion for a decision on suitability for final disposal. Using non-destructive measurement techniques many nuclides in waste packages can be determined due to their characteristic gamma emissions coming out of the packages. In radioactive waste mostly complex mixtures of alpha-, beta-, gamma-emitting nuclides are present and chemical separations have to be performed prior to radiometric analysis of these nuclides.

At KFA Jülich rapid and non-labour intensive methods are studied for the dissolution of samples of cemented low level waste. The need for the development of new dissolution methods results from the fact that analytical measurement of about 60 nuclides are required by the waste acceptance requirements of BfS (1). The radionuclide inventory of the resulting solutions is determined by alpha- and gamma-spectroscopy and Liquid Scintillation Counting. The latter only measuring the total content of photon producing radioactive radiation.

Former dissolution experiments using hydrochloric or nitric acid clearly demonstrated that powdered cement samples in most cases will not be completely dissolved so that radioactivity will be partitioned between the solution and undissolved residue. Moreover the solutions tended to gel making filtration, a really time consuming task, necessary.

Using a laboratory microwave oven for the dissolutions (2) therefore seemed to be a promising way to better results because higher temperatures and pressures could be applied and energy would be more efficiently transmitted to the sample. Moreover the microwave dissolution vessel represents a closed system so that volatile elements cannot escape.

Radiometric measurements often can be complicated by the fact that an abundant nuclide interferes with the nuclide of interest. To avoid time consuming radiochemical separation procedures like extraction or precipitation decision was made to use the High Performance Liquid Chromatography (HPLC) (3). Under appropriate conditions the separation of Fe, Co, Ni, Mn should be possible within less than 30 minutes.

EXPERIMENTAL

The samples to be dissolved were taken from a block of Portland Cement which previously had been blended with Fe, Co, Ni, Mn, Ce and Sr in such a way that 26 ppm(wt) of each of these elements were added to the unknown natural elemental concentrations in the cement. The samples were grinded with a ring-roller mill to particle sizes smaller 100 μm . For the extractive dissolutions a Soxhlet apparatus was used and for

the reflux experiments usual laboratory glass equipment. The microwave experiments were carried out in a laboratory microwave oven (model MLS 1200, supplier BÜCHI, Göttingen, Germany) equipped with a reaction vessel container for six units. The reaction vessel (Fig. 1) is manufactured from TEFLON and can be applied for pressures up to 120 bars. For safety reasons it is equipped with a plate spring relief valve and additionally surrounded with a protective cover.

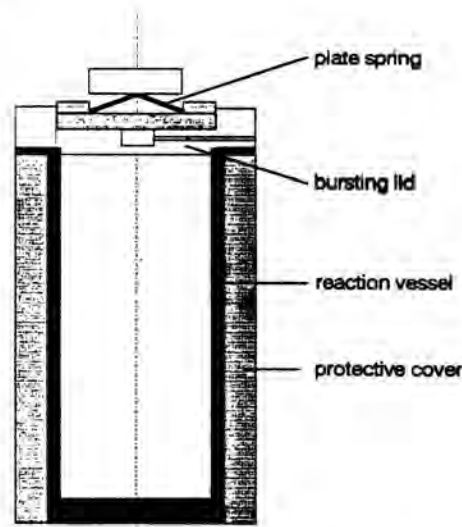


Fig. 1. Schematic drawing of the microwave reaction vessel.

In each extraction and reflux experiment 1000 mg of the grinded cement sample were reacted with 50 ml of the solvents (H_2O , HCl , HNO_3) up to 4 hours. Experimental conditions for the microwave experiments are given below.

sample amount	200 mg
nitric acid(3M)	10 ml
sodium fluoride	50 - 100 mg
microwave energy	250 W
heating time	15-20 min

A conventional HPLC-system is used for development and test of chromatographical separation procedures. For the separation tests of uranium and transition elements a silicagel based cation exchange-column (type Nucleosil 5SH) was used. The mobile phase consisted of two 0, 15 M tartaric acid

solutions of different pH. The initial composition of the solvent was increased from pH=2, 8 to pH=4, 0 by a programmed gradient. To avoid possible contamination, pressure exposed parts are manufactured from PEEK (polyetheretherketone). Sample injection is performed either manually or by an autosampler. The injection volume was 50 μ l. A UV-VIS-detector was used for the detection of non-radioactive elements. A computer controlled sample collection system is additionally installed for the collection of the separated fractions leaving the column.

RESULTS ON DISSOLUTION

Dissolution tests on cement samples with H₂O, HCl and HNO₃ were carried out under reflux conditions, by Soxhlet extraction and microwave digestion. From the data of Table I it can be derived that an almost complete dissolution can only be achieved under reflux conditions with inorganic acids. As already mentioned earlier the cement samples had been doped with 26 ppm of each of the elements in the table. This concentration could be verified for Ni, Co and Ce which are obviously not constituents of our cement in contrast to Fe, Sr, and Mn which are already part of the matrix cement. This could be proved by ICP-AES analysis. Although analytical results under reflux conditions are satisfactory the dissolving procedure is rather time-consuming and filtration is strongly hampered by the inevitable formation of silicic acid gel.

First dissolution experiments with hydrochloric acid (3M) and nitric acid (3M) in a microwave oven showed that only negligible parts of the cemented product remained undissolved. Gelling, however, due to the formation of silicic acid still occurred being minor with nitric acid. It was therefore considered to add sodium fluoride in order to suppress the gelling process due to the formation of SiF₆⁻ ions. Under the above conditions samples of cemented waste could be decomposed in the microwave oven within 20 minutes to clear and stable solutions. Stability of the solutions (i.e. no gel formation) is found up to three months at room temperature. Even greater stability of the solutions is found when stored in a refrigerator at approx. 5°C. Samples stored in this way for more than one year could be analyzed without any pretreatment leading to comparable results as with freshly prepared samples. Obviously, microwave digestion of the cement samples is the most rapid and effective procedure followed by boiling under reflux with nitric acid (3M). The latter procedure, however needs about 4 h compared with approximately 20 minutes for the microwave method.

RESULTS ON SEPARATION

If complex mixtures of nuclides are present in a solution, HPLC offers an effective means for their separation. This is particularly true for beta-emitting nuclides like Fe-55, Ni-63,

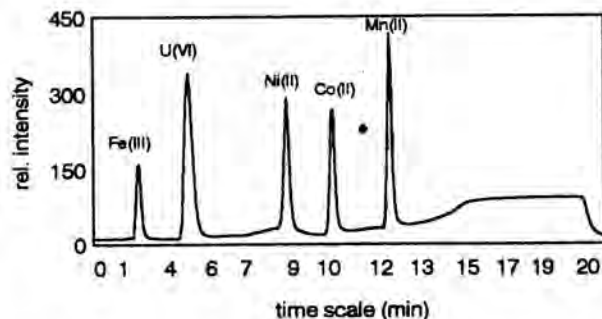


Fig. 2. Chromatogram of some transition elements and uranium.

Ca-45, Sr-90 etc. which cannot be measured by non-destructive methods. Figure 2 shows a chromatogram of transition elements including uranium. The chromatogram actually represents the UV-detector signals for the separated elemental fractions. For the determination of the radioactive amount of an element (e.g. Fe-55 in the Fe-fraction) the single elemental fractions are collected in small vials directly suited for LSC analysis. Radioactivity per 50 μ l-injection into the HPLC-system is generally lower 100 Bq per peak. Determination on recovery yielded 80 - 90% of the activity injected. For waste relevant accuracy of the radiometric measurement following the chromatographical separation 500 Bq per 50 μ l injection were estimated sufficient.

CONCLUSION

Microwave dissolution and High Performance Liquid Chromatography are components of a fast, reliable and flexible laboratory system for the analysis of radionuclides not accessible to non-destructive testing. Quantification of nuclides is achieved in much shorter time as compared with conventional radioanalytical procedures. A major advantage of the HPLC method is the opportunity of measuring radionuclides free from interferences thus facilitating the determination of nuclide correlations.

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TABLE I
Results of Dissolution Experiments on Cement (by ICP-AES)

Solvent	Dissolution Conditions	Time h	Fe ppm	Ni ppm	Co ppm	Mn ppm	Ce ppm	Sr ppm
H ₂ O	Extraction	4	0.07	0.1	0.04	0.006	0.3	29
HCl,3n	Extraction	4	285	6.7	6.4	13	6.8	61
HNO ₃ ,3n	Extraction	4	330	9.1	9.1	19	9.9	86
HCl,3n	Reflux	4	1260	26	25	51	27	170
HNO ₃ ,3n	Reflux	4	1330	27	27	54	29	180
HNO ₃ ,3n	Microwave	0.3	1350	27	28	57	32	174

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