

Combined procedure for the determination of ^{90}Sr , ^{241}Am and Pu radionuclides in soil samples

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A combined procedure for sequential determination of low level activity concentrations of ^{90}Sr , ^{241}Am and Pu radionuclides is described. The analysis of α -emitters is performed by isotope dilution α -spectrometry using ^{242}Pu or ^{236}Pu and ^{243}Am tracers. Strontium-90 is analyzed by liquid scintillation counting using the double energetic windows method. The method combines the well established procedure for Pu analysis based on anion exchange, the powerful and selective method for Sr isolation based on extraction chromatography using Sr-Spec resin and finally it includes the application of the TRU-Spec column for separation and purification of the Am fraction. The radiochemical procedure was tested using IAEA reference and intercomparison materials. Major parameters of the procedure as well as advantages and drawbacks are discussed in detail.

Introduction

It is known that in the analysis of radionuclides in soils, problems related to inhomogeneity and particle size fractionation during sub-sampling arise.¹ Therefore, it is desirable to have a combined procedure that allows a more reliable activity concentration correlation from the same sub-sample or from the same unique sample.

This paper presents in detail the combined procedure used at the IAEA's Laboratories in Seibersdorf, Austria for determination of ^{90}Sr , ^{241}Am and Pu radionuclides in soils. Two sample dissolution methods have been applied: conventional wet digestion and high-pressure microwave digestion. The radiochemical procedure consists of a Pu separation step by anion exchange in 7-8M HNO_3 after oxidation state adjustment to Pu(IV).¹ Then a pre-concentration of Am and Sr by co-precipitation with calcium oxalate is performed. Am is separated from Sr by extraction chromatography using TRU-Spec resin. For further purification of the Am fraction (separation from REE) anion exchange chromatography is used. The final Sr separation and purification is performed by extraction chromatography using Sr-Spec resin.² Thin sources for Pu and Am determination by alpha spectrometry are prepared by micro-co-precipitation with NdF_3 .

Experimental

Sample preparation

A flow chart of the entire chemical procedure is shown in Fig. 1.

Drying and ashing

Dry-to-wet mass ratios were determined on separate sub-samples of about 1-2 g, which were dried for 2 h increments in shallow porcelain dishes at 105 °C until the weight remained constant. Typical amounts of 100 g were

ashed in porcelain dishes in a large electric muffle furnace with a gradual heating program up to 600 °C.

Wet destruction using mineral acids and conventional wet destruction

Ten g of ash are weighed into a Teflon beaker and mixed with 10 ml 1M HNO_3 to produce slurry. Ten 10 mg of strontium carrier and spikes of ^{243}Am (0.014 Bq) and either ^{236}Pu or ^{242}Pu (0.017-0.1 Bq) tracers are added. The selection of the type and amount of Pu tracer depends on the expected activity concentration of the Pu nuclides in the sample. Because of the low activity concentration, ^{242}Pu is mainly used as radiochemical yield determinant in the present work. Spiked slurries and blank are stirred, digested and evaporated successively twice with (40-70 ml) 40% HF, three times with 50 ml 65% HNO_3 and with (30-50 ml) 32% HCl with 2-3 g of boric acid. The digestion residues are converted to nitrate form by evaporating three times with 10 ml 65% HNO_3 and dissolving in 70 ml 1M HNO_3 . If the resulting solution is visibly turbid or contains suspended solids, it is centrifuged. The insoluble component is treated according to strategies that bring about dissolution of commonly occurring residues such as silica and titanium dioxide. Certain mineral inclusions in soil, however, are resistant to attack.

Finally, the resultant liquid is passed through a 0.2 μm pore size filter. The filter with the undissolved residue is dried and measured for gross alpha beta activity.

High pressure microwave digestion

Ten g of ash are weighed into a 500 ml Teflon bomb container and mixed with 20 ml 65% HNO_3 , 20 ml 40% HF and 5 ml 65% HClO_4 . The tracers and Sr carrier are also added in the same proportions as used for the conventional destruction. A high performance microwave digestion unit (MLS 1200 MEGA) is used. The microwave program used is shown in Table 1.

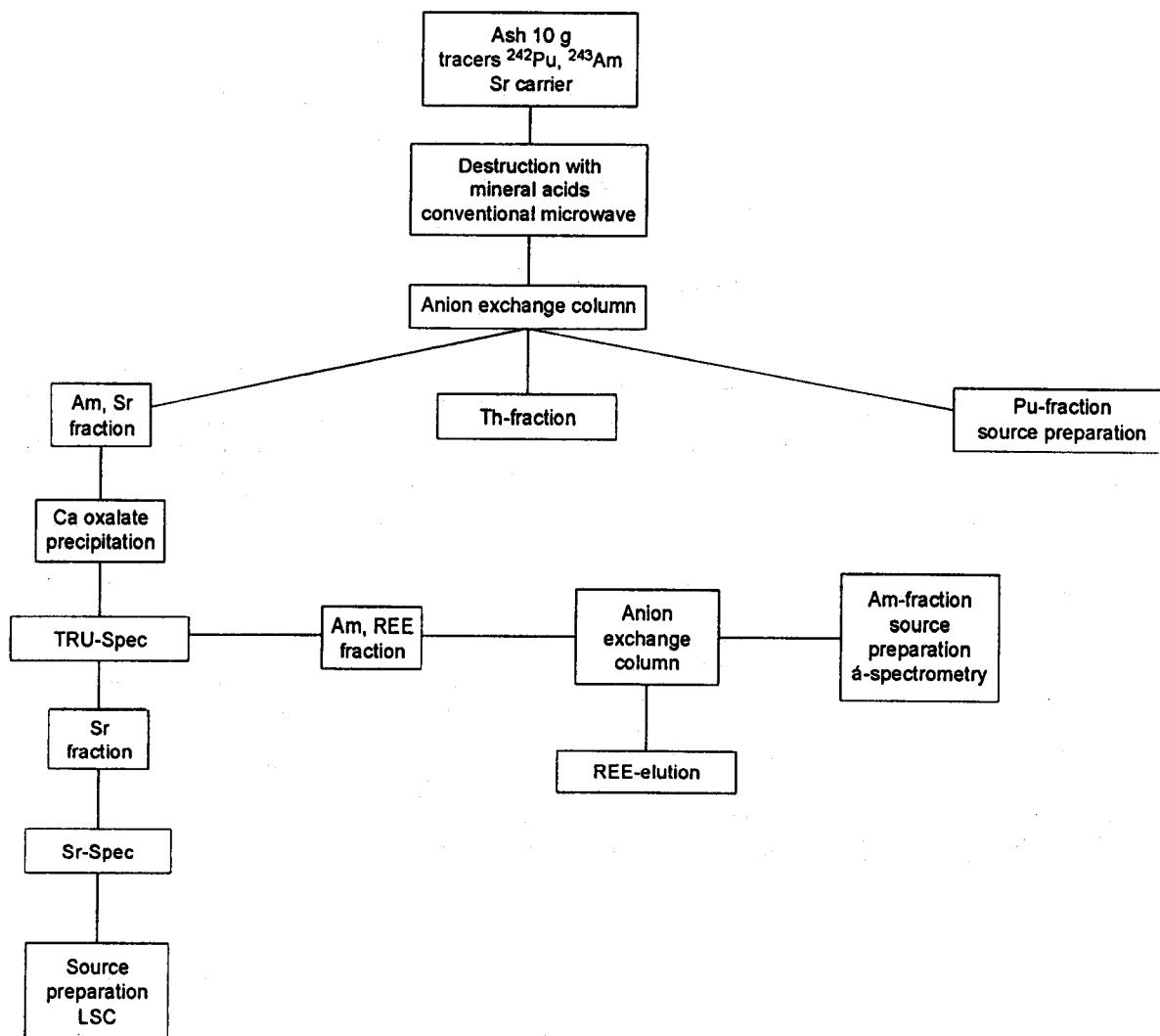


Fig. 1. Flow chart of combined procedure for the determination of ^{90}Sr , ^{241}Am and Pu radionuclides in soil samples

The program is repeated after the addition of the same amounts of HNO_3 and HF. If a black residue still remains at the bottom of the container, the microwave procedure is repeated again without the addition of further amounts of reagents. Usually a white colloidal residue (silica, fluorides such as CaF_2 and compounds of titanium and other transition metals) remains after the microwave digestion. At this stage, all the solution and any suspension is transferred to a cleaned Teflon beaker. The digestion residue is evaporated to dryness three times with 10 ml HNO_3 (65%), digested with 50 ml HCl (32%)/3 g of H_3BO_3 and evaporated to dryness. The succeeding steps are the same as it is described earlier.

Table 1. Microwave program

Steps	1	2	3	4	5	6	7 Cooling
Time, min	5	0.5	5	5	2	5	10
Power, W	250	0	250	400	400	500	0

Plutonium separation by ion exchange and plutonium oxidation state adjustment

The oxidation state of Pu is adjusted to tetravalent: Pu and Fe(III) ions in less than 1M HNO_3 solution are reduced to Pu(III) and Fe(II), respectively, using 0.5–1.5 ml of 100% hydrazinium hydroxide. The completeness of the reaction is tested by adding one drop of 1M NH_4SCN solution to 1-2 drops of sample solution on a spot plate. The resulting ferrous ions together with some excess of hydrazinium hydroxide will rapidly convert all soluble Pu species to the trivalent oxidation state. Then, 30 ml of 65% HNO_3 are added and the solution heated to destroy the excess of hydrazinium hydroxide. Samples are cooled and 2-3 g of sodium nitrite are added to ensure conversion of Pu(III) to Pu(IV). The excess of nitrous acid consumes any remaining hydrazine but has to be destroyed before passing the solution through the anion exchange column by gently boiling (1-2 minutes) the solution which is about 4M HNO_3 . Seventy ml of 65% HNO_3 are added to the

cooled solution to adjust the acidity of the solution to about 8M. The volume of this solution is now about 200 ml.

Anion exchange separation of Pu(IV)

Columns are prepared from Bio Rad AG 1-X8 (mesh 100-200) resin in the chloride form. Inner diameter: 10 mm, resin bed length: 140 mm. Columns are conditioned with 50 ml 8M HNO_3 . Sample solutions are loaded into the column followed by washing with 50 ml 8M HNO_3 . The combined effluent is used for the analysis of Am and Sr nuclides. Columns are washed with 100 ml 10M HCl to desorb Th. Finally, Pu is stripped with 100 ml 0.1M NH_4I -9M HCl solution. The iodide reduces Pu(IV) to Pu(III), which does not form an anionic chloride complex. Any Np(IV) and U(VI) are retained by the resin column since they are not reduced by iodide.

Plutonium source preparation by micro co-precipitation technique

The Pu strip solution is evaporated to dryness after the addition of 1 ml of 5% NaHSO_4 . Ammonium iodide is destroyed by evaporating 3 times with 2 ml 65% HNO_3 and the final residue is taken up in 20 ml 1M HNO_3 . Pu is reduced to trivalent state with 100 mg of Mohr's salt, $(\text{NH}_4)_2\text{Fe}(\text{II})(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. Under these conditions some of the U is possibly reduced to tetravalent state by Fe(II). Then, Pu(III) is oxidized to Pu(IV) and any U(IV) to U(VI) by adding 1 ml of NaNO_2 (25%). Following this procedure the co-precipitation of U is minimized.³ Pu is finally co-precipitated on NdF_3 adding 50 μg of soluble Nd salt and 5 ml 40% HF to the solution. After 30 minutes the neodymium fluoride suspension that carries the alpha activity is filtered through a 25 mm, 0.1 μm membrane filter (Metricel polypropylene, Gelman Sciences), dried and mounted on a stainless steel disc and analyzed by α -spectrometry.

Pre-concentration of Am and Sr by co-precipitation

The combined effluent from the anion exchange column is evaporated to about 20 ml and diluted to 150 ml with double distilled water. Ten g of oxalic acid are added and the pH of the solution is adjusted to 5.5-6.0 with 25% ammonia so that both Am and Sr are co-precipitated. Under these conditions in many cases, most of the Fe remains in solution in the form of oxalate complexes. The precipitate is centrifuged and washed with 25 ml double distilled water three times. The oxalate precipitate is destroyed by evaporation with 65% HNO_3 (3×10 ml).

Separation of Am and lanthanides using TRU-Spec column

The residue is taken up in 20 ml 2M HNO_3 . The content of Fe(III) is tested by adding one drop of 1M NH_4SCN solution to 1 drop of sample solution on a spot plate. If the

test is positive (red color) up to 300 mg of ascorbic acid is added to the solution to reduce Fe(III).

The columns are prepared from TRU-Spec resin. Bed volume of 1.3 ml, column length: 26 mm. Columns are conditioned with 25 ml 2M HNO_3 . Samples are loaded to the column followed by washing with 10 ml 2M HNO_3 . The combined effluent is used for the analysis of Sr nuclides. The column is washed with 4 ml 9M HCl and finally Am together with the lanthanides are stripped with 15 ml 4M HCl solution. The traces of Th and U that might be present remain on the column providing a further purification of the Am fraction.

Separation of Am from lanthanides by ion exchange

The 4M HCl solution is evaporated to dryness and converted to nitrate with 65% HNO_3 (3×1 ml). The residue is taken up with 10 ml 1M HNO_3 -93% CH_3OH . Columns are prepared from Bio Rad AG 1×4 (mesh 100-200) resin. Inner diameter: 10 mm, column length: 120 mm. Columns are conditioned with 100 ml 1M HNO_3 -93% methanol. Samples are loaded onto the columns followed by washing with 20 ml 1M HNO_3 -93% methanol. Columns are washed with 80 ml 0.1M HCl-0.5M NH_4SCN -80% methanol to remove the lanthanides. A wash with 20 ml of 1M HNO_3 -93% methanol is performed. Am is stripped with 70 ml 1.5M HCl-86% methanol solution.⁴

Am source preparation by micro co-precipitation technique

The strip solution is evaporated to dryness after the addition of 1 ml of 5% NaHSO_4 . Any organic is destroyed with 2 ml 65% HNO_3 ($3 \times$). Am salt is taken up with 20 ml 1M HNO_3 and co-precipitated with NdF_3 adding 50 μg of soluble Nd salt and 5 ml 40% HF to the solution. Co-precipitated Am is filtered through a 0.1 μm membrane. Mounted membrane filters are analyzed by α -spectrometry.

Separation of strontium with Sr-Spec

About 3 ml 65% HNO_3 are added to the combined effluent of the TRU-Spec column to turn it to 3M. Columns are prepared from 3 g Sr-Spec supported crown ether. Inner diameter: 10 mm, column length: about 100 mm. Columns are conditioned with 100 ml 3M HNO_3 . Sample solutions are loaded to the column, then the columns are washed with 100 ml 3M HNO_3 to remove most of the alkaline earth metal interferences. Sr is stripped with 30 ml distilled water.

Sr source preparation by precipitation

Three hundred mg of oxalic acid are added to the strip solution. Strontium oxalate is precipitated from alkaline solution by adding 3 ml 25% NH_3 (pH 9-10). The

precipitate is filtered through pre-weighed filter paper. The chemical recovery for strontium is determined by gravimetry and/or ICP-ES. Samples are dissolved in 1 ml 1M HNO₃ and mixed with 15 ml Insta Scint-Gel Plus scintillation cocktail. Strontium-90 is analyzed by liquid scintillation counting.

Alpha-spectrometry

The α-spectrometry measurements were carried out with Canberra PIPS (passivated ion implanted planar silicon) detectors. The spectrometers (Tennelec model TC257 and EG & G Ortec models 676 and 676A) were connected by a multiplexer (Canberra Model 8224) to an ADC (Canberra Model 8701) and to an AIM (Canberra Model 556) using a computer IBM 350 (Canberra Genie PC software).

The isotope dilution method is applied. The disintegration rate of the analyte activities in each sample is calculated on the basis of the known tracer activities added to the sample. The ratio of the α-spectral peak areas (analyte/tracer) after corrections for background, tailing (when using ²³⁶Pu as tracer) and reagent blank is taken to be equal to the ratio of the disintegration rates.

Beta-scinillation counting

The determination of the activity concentration of ⁹⁰Sr is performed using the double energetic windows method.

The first energetic window includes all the ⁹⁰Sr spectrum and the low energy region of ⁹⁰Y spectrum. The window B includes the high energy region of ⁹⁰Y spectrum. Strontium-90 activity is determined by subtracting the contribution of ⁹⁰Y in region A from total counting rate in this region.

Results and discussion

Comparison with references values and results are shown in Tables 2 and 3. The activity concentrations of ^{239,240}Pu are all within the confidence interval except IC/test-1/MW and IAEA-375/CD/C (Table 2). Most of the ²³⁸Pu activities are below the minimal detectable activity. Results of ²³⁸Pu activity concentration in IAEA-375 fall into the confidence interval of the information value. Only for IAEA-375/CD/C one abnormally high value was obtained.

Unfortunately for these materials there are no currently existing reference values for Am concentrations. Most of the ²⁴¹Am results are within the given information value confidence interval (Table 3).

Chemical recoveries and spectral characteristics

The chemical recoveries for Pu are usually higher than 80% and show a narrow dispersion. The α-spectra from the Pu fractions have good resolution (50–70 FWHM) and show neither Th nor U contamination.

Table 2. Plutonium results in some (present/future) IAEA reference materials

^{239/240} Pu					²³⁸ Pu			
Sample/method	n	Mean concentration, Bq/kg dry	Chem. rec., %	Recommended (info)value	n	Mean concentration, Bq/kg dry	Chem. rec., %	Recommended (info)value
IAEA-326/MW	2	0.49 ± 0.04	86 ± 6	0.49	2	< 0.036	88 ± 6	0.019
IAEA-326/CD	4	0.47 ± 0.03	93 ± 6	0.48–0.51	4	< 0.036	93 ± 6	0.017–0.022
				IAEA/AL/100P				IAEA/AL/100P
IAEA-327/MW	3	0.57 ± 0.04	81 ± 5	(0.58)	3	< 0.036	81 ± 5	0.020
IAEA-327/CD	4	0.58 ± 0.03	92 ± 5	0.57–0.60	4	< 0.036	92 ± 5	0.018–0.023
				IAEA/AL/100P				IAEA/AL/100P
SOIL-6/MW	1	0.99 ± 0.03	64 ± 4	1.036	1	< 0.036	64 ± 6	
SOIL-6/CD	3	1.03 ± 0.04	95 ± 7	0.96–1.11	3	< 0.036	95 ± 8	no info
				IAEA/RL/111				IAEA/RL/111
IAEA-375/MW	1	0.34 ± 0.02	97 ± 6	(0.3)	1	0.09 ± 0.01	97 ± 6	(0.071)
IAEA-375/CD/A	7	0.29 ± 0.03	101 ± 7	0.26–0.34	3	0.07 ± 0.01	97 ± 6	0.056–0.085
IAEA-375/CD/B				IAEA/AL/075	4	0.057 ± 0.037	107 ± 10	IAEA/AL/075
IAEA-375/CD/C	1	0.54 ± 0.02	115 ± 7		1	0.23 ± 0.02	115 ± 7	
IC-test/MW	1	0.19 ± 0.02	87 ± 6	(0.074)	1	< 0.036	87 ± 7	(0.011)
IC-test/CD	3	0.08 ± 0.01	99 ± 6	0.068–0.085	3	< 0.036	99 ± 6	0.0033–0.0188

Estimated overall uncertainties at 1σ level.

MDA – minimum detectable activity.

n – number of experiments.

CD – conventional digestion.

MW – microwave digestion.

A – ²⁴²Pu is used as tracer, B – ²³⁶Pu is used as tracer, C – special case (see text).

Values in italics are preliminary results from intercomparison data (IC-test).

MDA = 0.02 Bq/kg for ^{239/240}Pu.

MDA = 0.036 Bq/kg for ²³⁸Pu (²⁴²Pu as tracer).

MDA = 0.05 Bq/kg for ²³⁸Pu (²³⁶Pu as tracer).

Table 3. ²⁴¹Am and ⁹⁰Sr results in some (present/future) IAEA reference materials

²⁴¹ Am				⁹⁰ Sr					
Sample/method	n	Mean concentration, Bq/kg dry	Chem. rec., %	Recommended (info)value	Sample/method	n	Mean concentration, Bq/kg dry	Chem. rec., %	Recommended (info)value
IAEA-326/MW	1	0.21 ± 0.03	32 ± 4	0.199	IAEA-326/MW	2	10.5 ± 1.1	49 ± 2	10.1
IAEA-326/MW*	1	0.20 ± 0.03	69 ± 5	0.161–0.238	IAEA-326/CD	4	11.2 ± 1.1	55 ± 3	0.96 ± 10.7
IAEA-326/CD	1	0.21 ± 0.06	14 ± 1	IAEA/AL/100					IAEA/AL/100
IAEA-326/CD	1	0.20 ± 0.03	24 ± 2						
IAEA-326/CD*	1	0.18 ± 0.06	47 ± 4		IAEA-327/MW	3	< 2.9	46 ± 2	2.39
					IAEA-327/CD	4	< 2.9	42 ± 2	2.25–2.53
IAEA-327/MW	1	0.20 ± 0.03	42 ± 3	0.22					IAEA/AL/100
IAEA-327/MW	1	0.27 ± 0.02	37 ± 2	0.189–0.252	SOIL-6/MW	1	28.2 ± 2.1	65 ± 3	30
IAEA-327/CD*	1	0.23 ± 0.02	68 ± 4	IAEA/AL/100	SOIL-6/CD	3	28.6 ± 2.1	62 ± 3	29–34
IAEA-327/CD	1	0.24 ± 0.03	30 ± 2						IAEA/RL/111
SOIL-6/MW	1	0.39 ± 0.11	12 ± 1		IAEA-375/MW	1	90 ± 6	91 ± 4	108
SOIL-6/CD*	1	0.45 ± 0.07	48 ± 4	no info	IAEA-375/CD/A	7	99 ± 6	76 ± 4	101–114
SOIL-6/CD	1	0.42 ± 0.04	27 ± 2	IAEA/RL/111	IAEA-375/CD/C	1	103 ± 6	65 ± 3	IAEA/AL/075
IAEA-375/MW	1	0.25 ± 0.03	75 ± 5	0.13	IC-test/MW	1	< 1.8	85 ± 4	1.4
IAEA-375/CD/A, B	7	0.16 ± 0.03	85 ± 5	0.11–0.15	IC-test/CD	3	< 1.8	89 ± 4	1.1–1.7
IAEA-375/CD/C	1	0.48 ± 0.03	86 ± 6	IAEA/AL/075					
IC-test/MW	1	< 0.01	67 ± 5	0.027					
IC-test/CD	3	0.03 ± 0.02	92 ± 7	0.020–0.035					

MDA – 0.01 Bq/kg dry.

*Ascorbic acid was used.

See Table 2 footnotes for explanation of symbols.

MDA = 2.9 Bq/kg (for IAEA-327).

MDA = 1.8 Bq/kg (for IAEA-375).

In the analysis of the chemical recoveries for Am (Table 3), a crucial point lies in the influence of Fe(III) on the Am uptake on TRU-Spec column. Following the separation procedure, part of the iron remains as soluble oxalate complexes in the filtrate after the calcium oxalate precipitation at pH 5.5–6. But some Fe co-precipitates with calcium oxalate. The amount of Fe depends on the chemical composition of the soil matrix.

In order to study the influence of Fe(III) in the retention of Am under dynamic conditions, experiments with synthetic solutions were conducted. Amounts of Fe in the form of Fe(III) between 50 and 300 mg were added to 20 ml of HNO₃ (1 and 2M) containing tracer amounts of ²⁴¹Am. The activity of the eluates was followed by liquid scintillation. Fractions were evaporated to dryness and mixed with 15 ml Insta-Gel. Duplicate experiments were performed: one without adding any reducing agent and one with ascorbic acid. The results indicate the strong influence of Fe(III) in the uptake of Am on the TRU-Spec column from HNO₃ (1 and 2M) solutions. Similar results are reported in the literature.⁵ Amounts of 100 and 800 mg of ascorbic acid were enough to reduce 50 and 300 mg of Fe(III) in nitric acid solutions, respectively. The total reduction of Fe(III) allows the maximum retention of Am on the stationary phase. Higher amounts of ascorbic acid should be avoided to prevent the formation of its decomposition products that lead to bubble formation and the interruption of the dynamic conditions.

The experiments with synthetic solutions provide a partial explanation of the wide range of values of chemical recoveries that were obtained for Am in the real samples. IAEA-375 contains about 90 mg of Fe per 10 g sample. In this case the reduction of Fe(III) to Fe(II) by ascorbic acid (100 mg) was seen to be complete on the basis of the negative test for Fe(III) with thiocyanate. For IC/Test 1 that contains 50 mg Fe per 10 g of sample, the situation was similar. For both soils, the recoveries for Am were always very high.

Soil-6, IAEA-326 and IAEA-327 contain higher amounts of Fe: between 200 mg and 270 mg per 10 g of sample. Table 3 shows that recoveries for these samples are generally lower than for IC/Test and IAEA-375 but when ascorbic acid is used, the chemical recoveries are improved. The alpha spectra from the Am fractions showed good resolution and no detectable interference.

In Table 3 the Sr chemical recoveries are presented. Recoveries are in the range of 42 to 91% after correction for the strontium content in the samples. Recoveries are regarded to be more or less acceptable considering that strontium sources are prepared in the last step of the combined procedure. Nevertheless, the following observations can be made: (1) replicates within a specific material type showed a narrow distribution of chemical recoveries and (2) between materials there is a wide variation, with relatively high recoveries for IAEA-375 and IC-test, acceptable recoveries for Soil-6 and lowest for

IAEA-326 and for IAEA-327. Low recoveries may be caused by the relatively low Ca content of IAEA-327 and IAEA-326. For samples containing low Ca content, the addition of several hundreds of mg of Ca carrier is recommended to carry down Sr more quantitatively during mixed Ca–Mg–Sr oxalate precipitation step.

Conclusions

The advantages of using MW compared to the CD are a shorter overall digestion period followed by evaporations to bring samples to a common point (HCl + H₃BO₃ step) in the destruction procedure (about 1.5-2 days for the MW procedure vs. 3-4 days for CD), use of lesser amounts of acids per sample and higher digestion temperatures than are possible at atmospheric pressure. However this technique requires the use of specialized equipment and a

sequential processing is needed for the analysis of 10 g samples.

The chemical recoveries for Pu are usually higher than 80%. Higher concentration of Fe interferes in the recovery of Am. Recovery of Sr has a wide range of 42–91%.

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