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DETERMINATION OF CESIUM, RUBIDIUM AND SCANDIUM IN BIOLOGICAL AND ENVIRONMENTAL MATERIALS BY NEUTRON ACTIVATION ANALYSIS

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A simple method for the determination of cesium, rubidium and scandium in soil, vegetation and animal tissues by neutron activation analysis has been developed and evaluated. The methodology was designed to enable the comparison of fallout radiocesium from Chernobyl with stable elements in radioecological studies. Sample materials are dried and homogenized, and aliquots are irradiated, in sealed polyethylene vials (ca. 0.5 cm^3), for 7 hours at a reactor flux of ca. $3 \cdot 10^{12}$ $n \cdot cm^{-2} \cdot s^{-1}$. The activation products of interest have long half-lives, and are analyzed by high resolution γ-spectrometry after a cooling time of at least 12 days. The practical lower limits for determination of Cs, Rb and Sc are 3, 7 and 0.13 $\mu g \cdot kg^{-1}$ for soils and 10, 20, 0.4 $\mu g \cdot kg^{-1}$ for biological materials, respectively. Measurement of scandium levels in vegetation allows a straightforward correction to be made for soil contamination. Various applications to soil-grass-animal ecosystems are described.

The contamination of large areas of Europe by radioactivity from the Chernobyl reactor accident (April 1986) has prompted extensive monitoring of the long-lived radiocesium isotopes, ^{137}Cs and ^{134}Cs, in a wide variety of ecosystems.[1] Whilst such data can be applied directly to establish control measures designed to limit human radiation exposure, for example from the consumption of food,[2] a full understanding of the behavior of a pulse-type input of a radioisotope to a complex ecosystem requires complementary information on the distribution and behavior of the corresponding naturally occurring element,[3] in this case ^{133}Cs. The analytical techniques reported in this paper were developed to support such investigations, and we have previously reported the application of Cs–NAA in a study of cesium metabolism in sheep,[4] and other radioecological studies of Chernobyl fallout.[5–8]

The determination of cesium in biological, geological or other environmental materials is notoriously difficult for many of the techniques commonly available for other trace elements in such materials,[9] with the exception of ICP–MS.[10] Cesium is an element of low natural abundance, generally ca. 0.1 $mg \cdot kg^{-1}$, in soil, ca. 0.01 $mg \cdot kg^{-1}$

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Table 1
Neutron activation properties for Cs, Rb, Sc

	Cs	Rb	Sc
Target nuclide	^{133}Cs	^{85}Rb	^{45}Sc
Isotopic abundance, %	100	72	100
Neutron cross-section, 10^{-28} m^2	26.5	0.41	16.9
Activation product	^{134}Cs	^{86}Rb	^{46}Sc
Half-life, day	736	18.7	83.8
Gamma energies, keV	796 (85)	1077 (8.8)	889 (100)
(branching ratio, %)	605 (98)		1120 (100)

in plants and animals, and below 0.001 $mg \cdot kg^{-1}$ in natural waters. Furthermore, because cesium is highly electropositive and has the lowest ionization energy of any element (with the exception of francium), electroanalytical techniques are not applicable, and for both atomic absorption and emission spectrometry sensitivity is very poor. However, the relatively large neutron cross-section of the only naturally occurring isotope, ^{133}Cs (see Table 1), and the long half-life of the primary activation product (^{134}Cs), means that neutron activation analysis can offer a potentially convenient, sensitive and specific means for the determination of total cesium in a wide range of substrates. Furthermore, the neutron activation requirements for the determination of cesium allow for straightforward and simultaneous determination of rubidium and scandium, which are of particular interest in this context, the former because of its chemical similarity to Cs, and the latter as a means of compensating for soil contamination of biological materials.

In this paper, we describe the development and performance characteristics of neutron activation analysis for cesium, rubidium and scandium in substrates typical of investigations in chemical ecology: soil, plant and animal tissues and excreta.

Experimental

Sample and calibration materials: The samples analyzed and recommended sample preparation are summarized in Table 2. Aliquots of dried, homogenized samples were accurately weighed into standard polypropylene vials (ca. 1.75 cm × 0.6 cm diameter, approximate volume 0.5 cm^2), so as to fill the vial. Accurate volumes of liquid samples (e.g., urine, water samples) were pipetted directly into the polypropylene capsule and evaporated at 80 °C. Repeat aliquots were evaporated into the same capsule so as to maximize the total sample activated with the minimum risk of contamination. The vial cap was heat-sealed in place and vials were leak-tested by placing them in hot water.

Blank samples were prepared from empty vials, or vials into which doubly distilled, deionized water (the same number of aliquots) had been evaporated.

Analytical calibration was based on gravimetrically prepared solutions of cesium, rubidium and scandium chlorides (AR grade) dissolved in 0.1M nitric acid (AR) prepared with doubly distilled, deionized water. Calibration materials for NAA were

Table 2
Samples analyzed and sample preparation

Sample	Preparation prior to NAA
Soil	Air dried (60 °C) and ground
Vegetation	
Faeces	
Animal tissues	Ashed (450 °C)
Milk	Freeze-dried, or liquid evaporated into capsules
Urine	
Plasma	
Red blood cells	

prepared from bulked homogenized sample materials (soil or grass), spiked with aliquots of the calibration materials, and thoroughly mixed. Calibration materials were weighed into polythene vials and irradiated alongside the sample vials. Thus a number of multielement calibration standards were produced, having a wide range of concentrations. Their uniformity was established by replicate NAA. Analytical accuracy was tested by analysis of two interlaboratory reference materials for which reference levels of the three elements of interest have been established: (a) Podmore Red Clay P1033, previously used at the Department of Chemistry, Manchester;[11] and (b) a reference freeze-dried serum standard from Ghent, Belgium.

Neutron irradiation and γ-spectrometry: For method development and initial applications,[3–6] sample irradiation was carried out at the Northern Universities Research Reactor at Risely, UK (this reactor is now defunct, but two other similar facilities are still available in the UK) Later work has been carried out using the research reactor at IFA Kjeller, Norway.[7,8] The Risley Reactor operated at power levels of up to 10^{13} n · cm^{-2} · s^{-1}, although in our work, to prevent overheating of the polypropylene vials, reduced power levels (100 kW) were employed. Sample vials (as described above) were irradiated in standard aluminium cans ("A-cans"; 10 cm × 3 cm diameter or 13 cm × 6 cm diameter). The sample vials were packed into layers within each can, and for working analyses at least one calibrant was included in each layer of vials. The smaller A-cans hold up to 21 samples, the larger cans up to 150 samples. It is wise to select the type and number of samples to be irradiated in a single batch so as to achieve

the most efficient counting procedure. The half-lives of activation products of interest, the approximate counting times required, and the time available on counting equipment should be taken into consideration when planning the analysis.

Samples and calibrants were irradiated for 7 hours at $3 \cdot 10^{12}$ n $\cdot$ cm$^{-2} \cdot$ s^{-1}, removed from the reactor and stored, still in their A-cans, for a minimum of 12 days to allow short-lived activity products to decay to acceptable levels (the critical nuclides here are ^{24}Na and ^{82}Br). Of course samples can be counted after a decay time of a couple of days if short-lived nuclides are of interest (i.e. ^{42}K, ^{24}Na). Sample and calibration vials were unpacked from the cans and examined by γ-spectrometry in a calibrated geometry using a high purity germanium (HPGe) detector (Canberra–Packard N-type, 14% efficiency, 1.8 keV resolution). Spectra were collected on a 4096 channel MCA (Canberra model 30) and data analysis was performed on a PC–AT microcomputer using Spectran–AT software (Canberra Packard).

Results and discussion

Analytical development

The activation sensitivity and corresponding detection limits (mass) for the three elements studied are given in Table 3. On the assumption of sample masses of 0.3 g (soil) or 0.1 g (vegetable or animal materials), the detection limits per unit sample mass have been derived. Reproducibility (within batch) has been calculated from replicate samples irradiated in the same batch of (usually four) A-cans. Linearity of activation response is maintained over at least five decades of analyte elemental mass, upwards from the lowest measurable concentration (Table 3).

The independence of the cesium activation response with respect to the sample matrix was tested by the method of standard additions described above. A number of

Table 3
Performance characteristics of NAA for Cs, Rb, Sc

	Cs	Rb	Sc
Activation sensitivity,[a] Bq $\cdot$ μg^{-1}	500	1 000	11 000
Detection limit,[b] ng	1	2	0.04
Determination limit, μg $\cdot$ kg^{-1}			
Soils	3	7	0.13
Biological samples	10	20	0.4
Reproducibility,[c] ± %	4	10	4

[a]Approximate activity generated after irradiation for 7 hours at a neutron flux $3 \cdot 10^{12}$ n $\cdot$ s$^{-1} \cdot$ cm^{-2}.
[b]Based on 12-hour count time.
[c]Within batch variability.

aliquots of each substrate were prepared, and spiked incrementally with increasing amounts of cesium chloride. No significant variation in the activation achieved with a particular level of cesium spike was observed across the range of substrates examined. In addition, no significant spatial variation in activation response was observed between the vials in an individual A-can, nor between the four small A-cans irradiated simultaneously in one batch.

The accuracy of measurement was tested by analysis of the Podmore Red Clay reference material and the Ghent serum standard, and satisfactory agreement (within 5%) was obtained for the three elements.

An irradiation time of seven hours was used, largely because this was a convenient period in relation to the reactor operational shifts and loading procedures in use at Risely. This irradiation resulted in the production of ca. 500 Bq ^{134}Cs per 1 μg ^{133}Cs, which in practice gave a suitable level of sensitivity for the analyses, given the typical concentrations of Cs found in the substrates being examined. Because of the long (2*y*) half-life of ^{134}Cs, longer irradiation could be used to produce proportionately increased specific activity if this were required. Alternatively, the mass of sample irradiated could be increased by ashing the samples or using larger vials.

Applications

Soil contamination of herbage

A major problem in the determination of fallout radiocesium in herbage (e.g., grass) is the possibility of cross-contamination by soil (e.g. from rain splash). The soil often contains radiocesium at concentrations 100 times or more than that of the grass from the same place, and a low level of soil contamination could generate grossly erroneous results. Although for a soil-plant-animal ecosystem it could be argued that the soil adhering to the plant is part of the animals' diet, the generally lower availability of radiocesium from soil than from plant materials makes the estimate of the level of soil contamination a matter of some importance.[12]

The determination of titanium has been used previously as a quantitative indicator of of soil contamination of plant material.[13,14] Both titanium and scandium are normally found in soil, largely as components of the clay fraction, but neither is incorporated into plants to any significant effect. Although titanium is by far the more abundant element, its neutron activation does not provide a convenient route for titanium analysis because of the short half-life (5.8 m) of ^{51}Ti. However, ^{45}Sc activates easily to ^{46}Sc, with long half-life and its measurement is straightforward (Table 1). Thus, the determination of scandium in both plant material and soil from the same location, together with determination of both natural and radiocesium in the soil, allows correction of the plant measurements for soil contamination.

Potential nuclear interferences in the determination of Sc using the $^{45}Sc(n, \gamma)^{46}Sc$ reaction arise from the fast neutron reaction on titanium, $^{46}Ti(n, p)^{46}Sc$. Fortunately, in practice, experience at URR indicates that this is insignificant unless epithermal irradiation conditions are used.

Natural cesium and radiocesium

The dynamics of incorporation of fallout radiocesium into natural ecosystems is readily followed by determination of both natural cesium and radiocesium in each compartment.[3–6] It is particularly convenient to determine environmental ^{137}Cs and ^{134}Cs by γ-spectrometry of the unirradiated sample, and the natural cesium by NAA. Except in rare cases (e.g., a sample where the radiocesium is present in the form of a highly radioactive or "hot" particle), the preactivation ^{134}Cs is no more than a small fraction of the postactivation level, and the errors introduced to the NAA determination of natural cesium by the presence of environmental ^{134}Cs are generally very small.

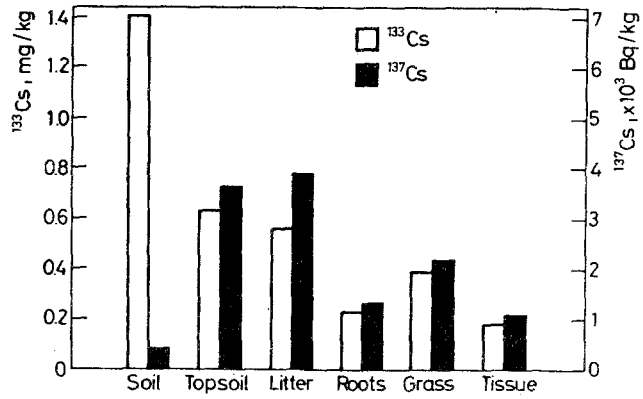

Fig. 1. Natural stable cesium and fallout cesium in an upland pasture ecosystem in Cumbria, UK, 1987

An example of this application is given in Fig. 1. Radiocesium (^{137}Cs and ^{134}Cs) and natural cesium concentrations were determined in soil, litter, vegetation and sheep tissues taken from a contaminated upland pasture in Cumbria, UK, in May 1987, one year after the deposition of Chernobyl fallout. The highest concentrations of ^{137}Cs were found in the litter layer, whereas the highest concentrations of natural cesium were found in the lower soil layer (2–5 cm) depth. A similar distribution pattern to natural cesium was observed for scandium, indicating that the natural cesium levels reflected the clay content of the soil samples. The similarity of isotope ratios in top-soil, litter, vegetation and sheep tissues (Table 4), shows that a dynamic equilibrium had been

achieved in that system, presumably through isotopic exchange, even though only partial penetration of radiocesium to deeper soil horizons had occurred by the time of the investigation.

The observed concentration ratios ($\mu g \cdot kg^{-1}$ veg/$\mu g \cdot kg^{-1}$ soil or $Bq \cdot kg^{-1}$ veg/Bq · · kg^{-1} soil) from the top soil (0–2 cm) to vegetation were similar for stable Cs and ^{137}Cs,

Table 4
Stable cesium and radiocesium in samples collected from an upland pasture ecosystem, Cumbria, UK, July, 1987 (Mean ± SEM, n = 10)

	^{133}Cs, $mg \cdot kg^{-1}$	^{137}Cs, $mg \cdot kg^{-1}$	$^{137}Cs/^{133}Cs$ $Bq \cdot \mu g^{-1}$
Soil (2–5 cm)	1.41 ± 0.21	420 ± 49	0.30 ± 0.06
Topsoil (0–2 cm)	0.63 ± 0.04	3620 ± 102	5.75 ± 0.40
Litter	0.56 ± 0.03	3910 ± 160	6.98 ± 0.47
Roots	0.23 ± 0.07	1320 ± 230	5.75 ± 0.92
Vegetation (grass)	0.39 ± 0.05	2180 ± 149	5.59 ± 0.81
Sheep (leg muscle)	0.18 ± 0.01	1090 ± 79	6.06 ± 0.55

i.e., 0.62 ± 0.11 and 0.60 ± 0.06, respectively. Therefore, the transfer of radiocesium from soil to vegetation, and the subsequent activities in the tissues of animals grazing these pastures, would only be reduced as radiocesium is translocated down the soil profile to the clay-rich, high Cs soils. With time, concentration ratios for radiocesium would be expected to decrease to a value approximate to that observed for stable cesium for the transfer from whole soil (0–5 cm) to vegetation (i.e., 0.28 ± 0.08).

Similar results have been reported following sequential extraction studies on Chernobyl-contaminated litter layer samples collected in Norway, 1989. Comparison of stable Cs: radiocesium isotope ratios in the different soil extractions indicated that isotopic exchange had been extensive.[7]

Intercomparison of potassium, rubidium and cesium

Because of the chemical similarity of these three elements, intercomparison of their behavior within the soil-plant-animal ecosystem is of considerable interest.[5,6] The elements follow the same uptake pathways and bind to the same sites, but competition for binding sites and different rates of membrane transfer can affect concentration ratios and transfer coefficients.[6] Simultaneous determination of rubidium and cesium by NAA (Table 1), and of potassium (as ^{40}K) by direct γ-spectrometry, is possible by our technique. Examples of this application are shown in Fig. 2, in which cesium and rubidium concentrations in the soil grass and animal components of a complex

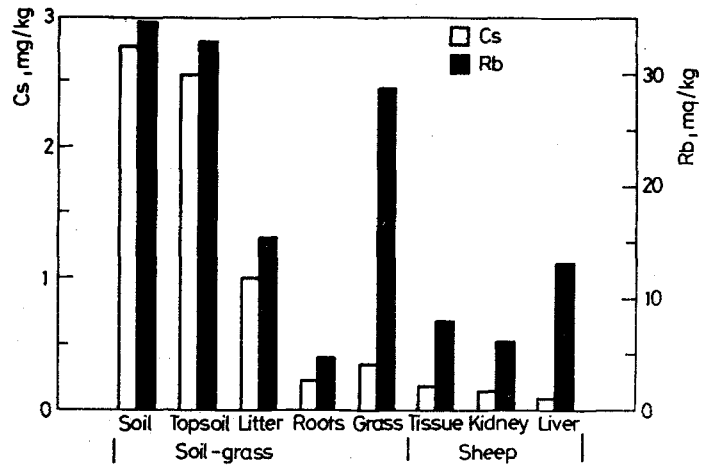

Fig. 2. Stable cesium and rubidium in an upland pasture ecosystem in Cumbria, UK, 1987

Table 5
Natural Cs, Rb ($mg \cdot kg^{-1}$) and ^{40}K ($Bq \cdot kg^{-1}$) concentrations in soil (0–5 cm) and grass samples from a lowland pasture, Cumbria, 1987. (Mean ± SEM, n = 10)

	Soil	Grass	Concentration ratio
^{40}K	500 ± 30	2250 ± 100	4.5 ± 0.4
Ru	24.5 ± 1.7	16.0 ± 0.6	0.65 ± 0.05
Cs	2.3 ± 0.4	0.21 ± 0.02	0.09 ± 0.02

Concentration ratio = concentration in grass/concentration in soil.

ecosystem are compared, and Table 5, which compares the soil to grass concentration ratios for potassium, rubidium and cesium. The decrease in concentration ratio, K > Rb > Cs, largely reflects the increase in binding strength of the hydrated ion to ion-exchange sites on soil components, i.e., the decrease in binding strength as one goes down the alkali metal group in the periodic table.

Conclusion

Cesium and rubidium may be determined at natural levels in soil and biological materials using neutron activation analysis on small samples (< 1 g) with minimal sample preparation.

The activated nuclides have long half-lives, and measurement by γ-spectrometry can be carried out after the decay of most of the short-lived activation products, so that low radiological exposure to the experimenter can be achieved.

The methodology is particularly suitable for the simultaneous study of radiocesium and natural cesium in ecosystem compartments.

Scandium in soil may be readily determined by the same technique, and scandium concentrations in vegetation may be used to correct for soil contamination.

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