

ANALYSIS OF CONTAMINANTS IN URANIUM COMPOUNDS BY POST-IRRADIATION PAPER CHROMATOGRAPHY

M. ÖRDÖGH AND V. UPOR-JUVAN CZ

Hungarian Academy of Sciences, Central Research Institute for Physics, Budapest (Hungary)

(Received April 4th, 1966)

INTRODUCTION

Partition paper chromatography has proved to be an adequate method for separating minute amounts of inorganic substances, that is why it is used more and more extensively for the identification of trace amounts of radioactive elements and it has been successfully combined with activation analysis in some cases^{1,2}. Our experience has also been that in the cases when a separation of the components of an irradiated sample is needed, paper chromatography is preferable to lengthy and laborious chemical precipitations because of the convenient and fast way in which adequate identification and evaluation can be achieved. It lends itself particularly well for the serial analysis of products when the accuracy requirements are not too high.

The chromatograms can be evaluated by autoradiography or G.M. counters, proportional counters, scintillation counters, etc. The chromatograms can be measured either individually, cutting into strips of 1 cm, or continuously by conveying them on a rail of 0.5 or 1 cm areas. This can most conveniently be done by using a counter assembly provided with an automatic conveyor and recorder³.

Paper chromatography can be combined with gamma-ray spectrometry, as first described by COULOMB for the determination of trace elements in ores^{4,5}. In this case the chromatogram is first measured by G.M. counter to establish the amount of activity present, then cut into strips, corresponding to the activity peaks and the expected R_F values of the elements in question, which are measured individually by gamma-ray spectrometry.

Three different methods have been developed at our laboratory for the determination of impurities in uranium compounds, *viz.* (1) chemical separation, (2) some chemical separation combined with gamma spectrometry, and (3) paper chromatographic separation. The first two of these methods have been already described^{6,7}, while the results obtained by paper chromatography will be reported presently.

EXPERIMENTAL

The activities produced by the irradiation of uranium compounds in a reactor are extremely high. To avoid the inconvenience of dealing with them, a method has been developed for the removal of the bulk of the uranium contained in the sample by paper chromatography before irradiation. Essentially, the procedure consists in

spotting the uranyl nitrate solution on filter paper in the form of a band, then chromatographing overnight with water-free ether containing 5 vol. % of nitric acid as solvent and using a descending overflow technique. Most of the uranium is thus carried away by the solvent while the contaminants do not move from the initial line. Some uranium is still left in the paper as manifested by an appreciable neptunium-239 activity produced by the irradiation.

As three drops of twice distilled water were used for rinsing the quartz ampoule when spotting the uranyl nitrate sample, the same quantity of water was spotted on to a paper blank processed simultaneously with the sample. After chromatographing with the nitric acid-ether solvent, strips of identical sizes were cut from both chromatograms, ashed and then irradiated simultaneously.

This method was preferred to the pre-irradiation separation techniques reported recently by other authors^{8,9}, namely, tributyl phosphate extraction or ion exchange. In our case the cations do not move in the solvent used, thus no other than the impurities present in the filter paper over the area of spotting will occur in addition to the sample contaminants.

In the experiments a uranyl nitrate solution containing known amounts of contaminants, made available by the courtesy of the I.A.E.A., was used. The half-lives of the isotopes and the gamma-energies involved in the measurements are listed in Table I.

TABLE I

LIST OF HALF-LIVES AND GAMMA-ENERGIES

Isotope	$T_{1/2}$	γ -Energy (MeV)
Chromium-51	27.8 d	0.32
Nickel (Co-58)	71.0 d	0.51; 0.80
Cobalt-60	5.27 y	1.17; 1.33
Copper-64	12.8 h	0.51
Manganese-56	2.58 h	0.84
Cadmium-115 (In-115)	53.0 h	0.335; 0.523
Molybdenum-99	67.0 h	0.141
Iron-59	45.1 d	1.10; 1.29
Sodium-24	15.06 h	1.38
Neptunium-239	2.3 d	0.106
Gold-198	2.69 d	0.411

The samples, in sealed quartz ampoules, were irradiated for 24 h by a $2 \cdot 10^{13}$ n/cm²·sec neutron flux from a VVR-S-type reactor. The corresponding standards were exposed simultaneously with the samples. Applying the usual method for post-irradiation chromatography, the samples were removed from the quartz ampoules by *aqua regia*, then heated on a water bath. After dissolving the sample, the nitric acid was removed by fuming and the samples reduced by evaporation to small volumes which were spotted on to 15 mm filter paper strips (Schleicher & Schüll 2043 A-type) and chromatographed by the ascending technique. Carriers were not added to the samples before spotting, but were directly spotted on to the chromatography strips. In order to obtain the quantitative transfer of the activated sample from the quartz beaker to the chromatography paper, the beaker was repeatedly rinsed with hydro-

chloric acid containing 15 to 20 μg inactive carrier of each of the contaminants in question.

For post-irradiation separation of the contaminants in samples of uranium compounds, a mixture of ethyl alcohol–hydrochloric acid–water (70:20:5) proved to be the most successful¹⁰. The chromatogram of a uranium sample is shown in Fig. 1. An activity measurement was performed for each cm of the chromatogram by means of a G.M. counter in a "Gamma"-type lead castle using 0.5 cm wide slits.

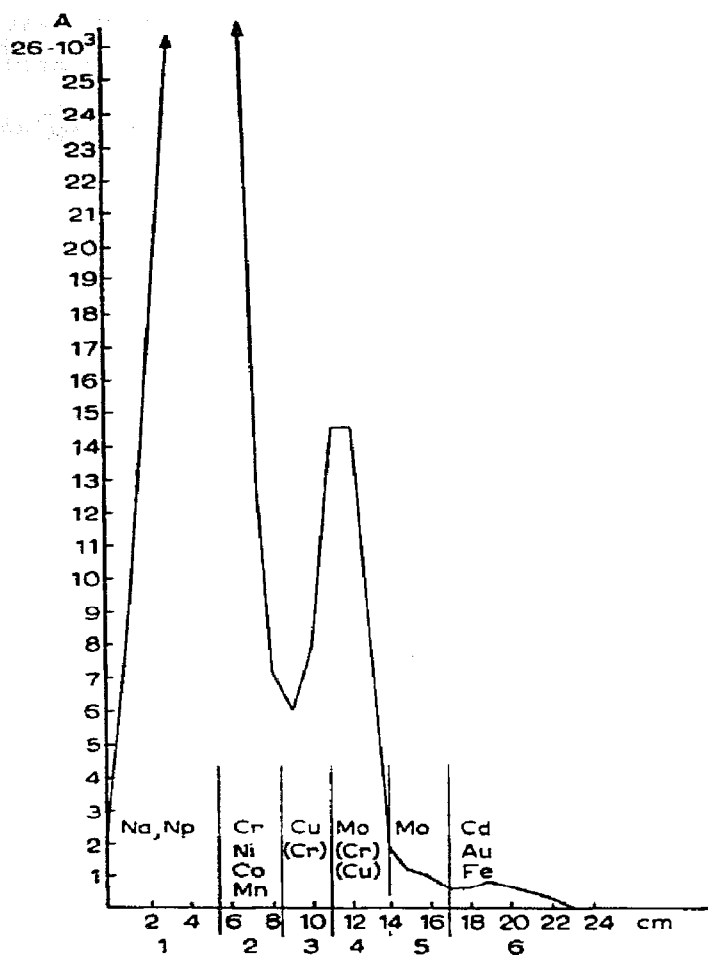


Fig. 1. Chromatogram of a uranium sample (No. 25): before cutting into sections, measured by G.M. counter.

The first 5 cm area of the chromatogram could not be evaluated from counts taken by the G.M. counter because of the presence of large sodium and neptunium activities in this strip. In the gamma-spectrometric measurements, however, the sodium and neptunium photopeaks can be, fortunately, well isolated. Section No. 2 contained cobalt, nickel, manganese and the major part of chromium present in the sample. Nickel was identified from the $^{58}\text{Ni}(n,p)^{58}\text{Co}$ reaction and was thus detected together with ^{60}Co . The major part of copper was detected in section No. 3, which contained some chromium as well. Traces of chromium were also identified in section No. 4, in addition to molybdenum and about 0.1 μg copper. The rest of the molybdenum

appeared in section No. 5. In the last section, *i.e.* section No. 6, cadmium, iron and gold could be identified. Measurements have been carried out with a Nuclear Enterprises crystal of 3 in. \times 3 in. NaI(Tl) and an EMI 9531 A photomultiplier tube together with a 128-channel Y-5-2-R type analyzer.

RESULTS AND DISCUSSION

The results of the chromatographic separation are listed in Table II.

The sample contained, apart from the expected contaminants, sodium, neptunium and gold. The rather high neptunium activity can be attributed to U-238 still left in the paper after the pre-irradiation chromatography. Sodium and gold could be detected both on the paper and in the uranyl nitrate solution. Experimental checks proved that these contaminants were present originally in the filter paper, mainly, while the sample contained only small fractions. The distribution of sodium had a fairly constant value, as seen from the comparison of the gamma-spectra taken for different runs, thus the sodium distribution over the filter paper seems to be, on the whole, uniform. Gold, on the other hand, was found to be unevenly distributed in the filter paper since the activities measured after different runs were found to be considerably different. Measurements on the paper blanks showed that the filter paper contained also some copper (*e.g.* about 0.7 μg in one of the blanks). Since copper was one of the contaminants, which we wanted to determine in the sample, the results of the activity measurement were corrected for the values measured on the corresponding blank.

The uranium left in the chromatography paper gives rise on irradiation not only to neptunium but also to activity due to fission products. Their kind and quantity have not been analyzed with the exception of molybdenum, the presence of which interfered with the analysis of the molybdenum contamination of the uranyl nitrate. An attempt was made to apply an appropriate correction by irradiating and chromatographing high-purity uranyl nitrate solution of about the same quantity as that of the uranium component of the sample and measuring subsequently the ^{99}Mo activity produced. It was not expected that wholly reasonable values would be

TABLE II
RESULTS OF THE CHROMATOGRAPHIC SEPARATION

Element	Run No. 25	Run No. 26	Run No. 29	Run No. 30	Mean value (μg)	Original amount (μg)	Difference (%)
Cr	11.43	14.75	10.1	10.94	11.81	9.825	+20
Ni	19.8	—	14.5	—	17.2	20	—14
Co	4.25	3.39	4.17	3.66	3.87	5	—22.5
Cu	4.70	4.47	2.89	5.07	4.28	5	—14.2
Mn	8.81	—	7.65	6.43	7.63	9.95	—23.2
Cd	0.18	0.19	0.17	0.22	0.19	0.5	—62
Mo	2.90	3.18	1.97	—	2.68	5	—46.3
Fe	17.40	—	30.3	38.8	28.8	49.45	—41.8
Na	+	+	+	+			
Np	+	+	+	+			
Au	+	+	+	+			

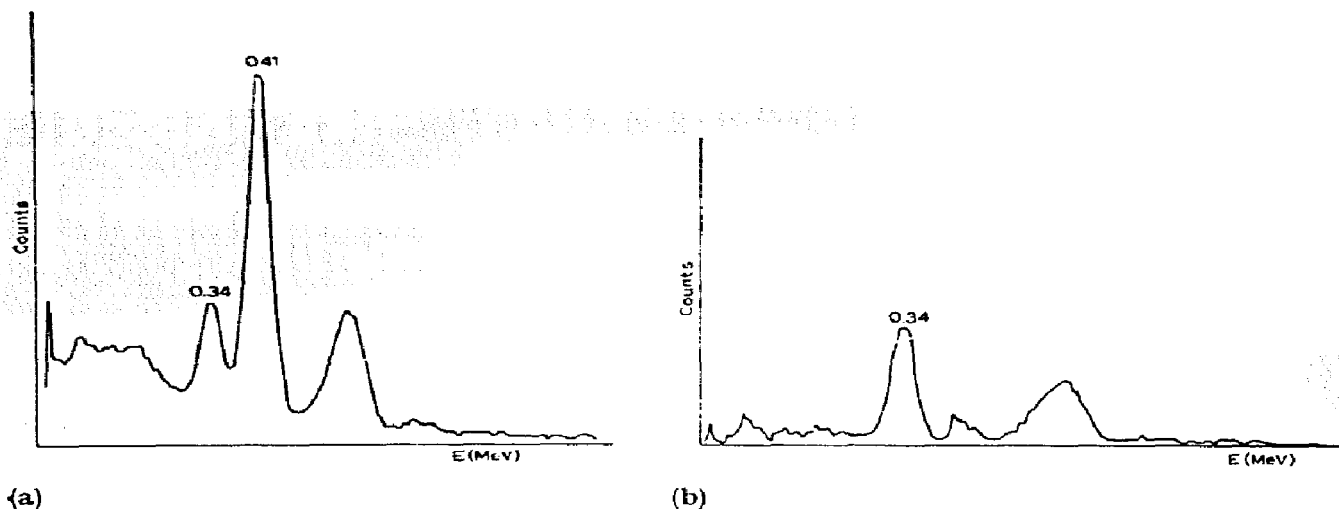


Fig. 2. Gamma-spectrum of chromatogram No. 30, section 17–24 cm. (a) Cd, Au; (b) Cd remaining after separation of Au by "complement subtraction" method.

obtained and we actually got in general about $2 \mu\text{g}$. The correction for this value induced, however, quite large negative errors in the measured value of the molybdenum contamination of the sample.

The error was fairly large in the cadmium determination too. Since in the solvent used for these experiments the R_F value of gold is very close to that of cadmium, the photopeaks of cadmium-115 cannot be isolated well from the considerable ^{198}Au activity present. In Fig. 2a the chromatogram area containing cadmium and gold is shown. The separation of gold was obtained from these gamma-spectra by the "complement subtraction" method (Fig. 2b).

Although iron is also included in the elements to be analyzed, its very poor sensitivity to activation analysis causes large errors in the determination.

The paper chromatographic separation is considerably more successful for the other elements listed in Table II. In Fig. 3, section No. 3 (8.5–11 cm) of the chromato-

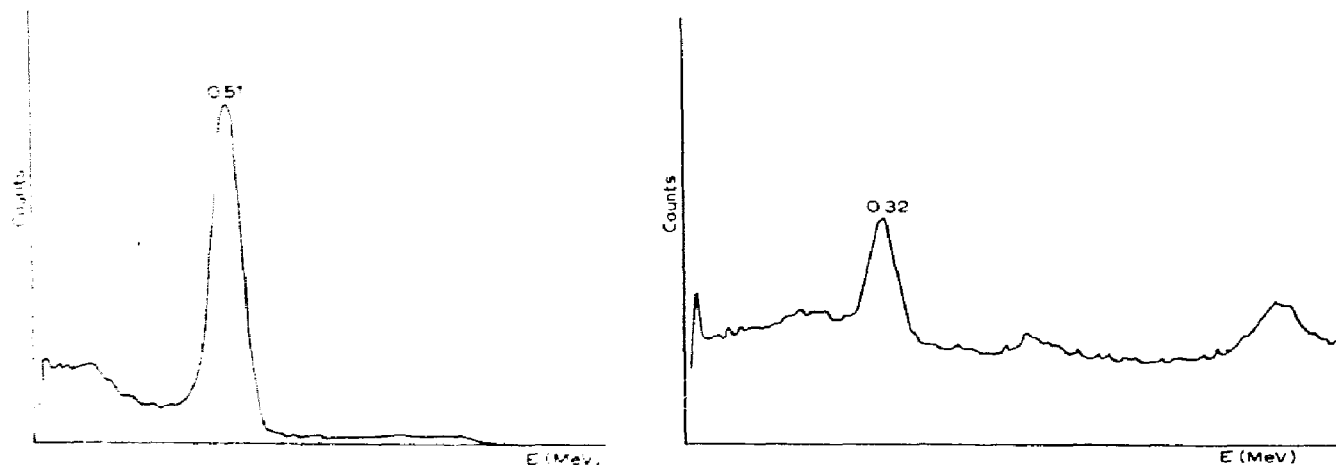


Fig. 3. Gamma-spectrum of chromatogram No. 25, section 8.5–11 cm: Cu.

Fig. 4. Gamma-spectrum of chromatogram No. 25, section 5.5–8.5 cm: Cr after 10 days.

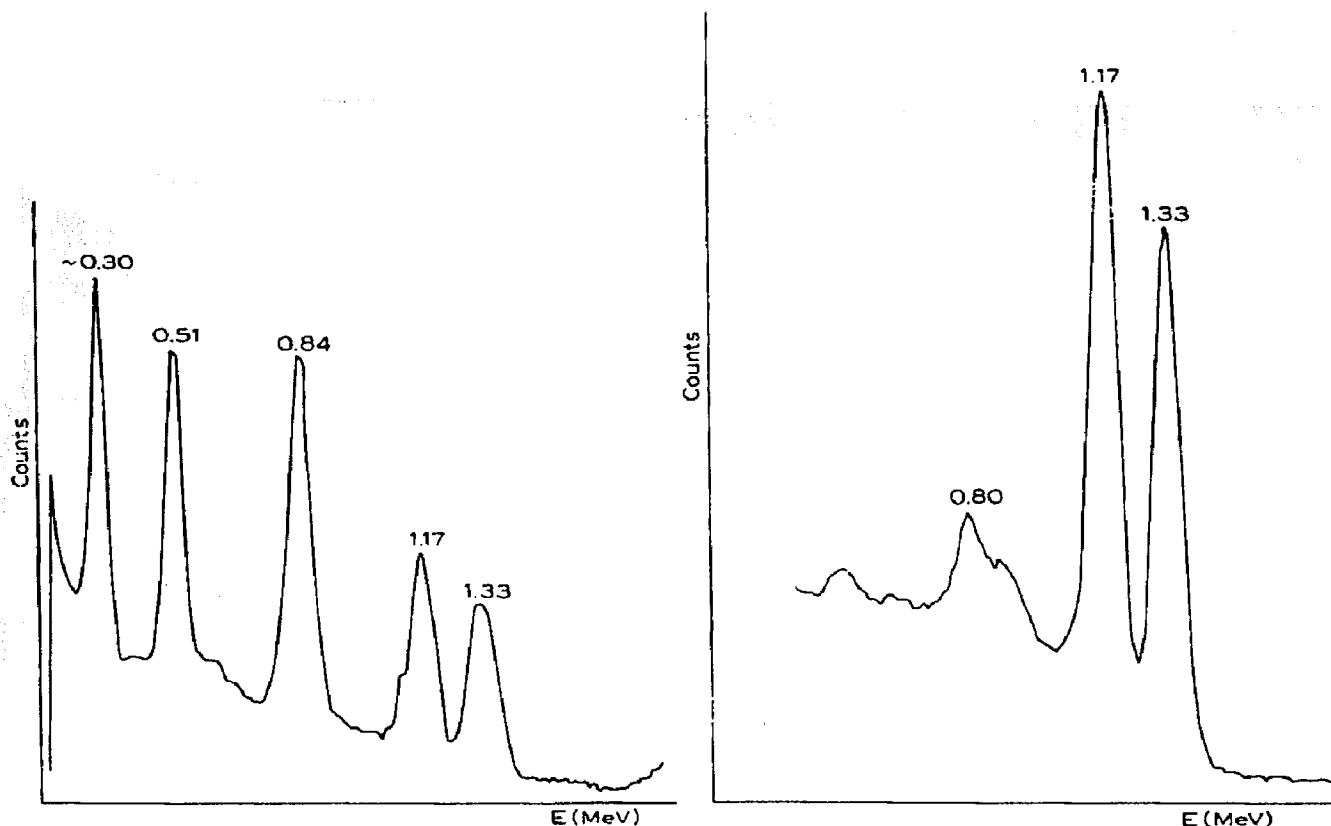


Fig. 5. Gamma-spectrum of chromatogram No. 29, section 8.0–11.5 cm: Cu, Mn, Co.

Fig. 6. Gamma-spectrum of chromatogram No. 29, section 6.0–13.5 cm: Co and Ni (^{58}Co) after two weeks.

gram shown in Fig. 1 is shown. It is apparent that copper can be measured without any inconvenience. Section No. 2 (Fig. 4), containing the majority of the chromium present, was measured after having been left to cool for about 10 days, so that most of the interfering elements had already decayed. In Fig. 5 the gamma-spectrum of an 8.0–11.5 cm strip of another chromatogram is shown. The picture was taken immediately after the chromatographic run. Though copper, manganese and cobalt appear together in this strip, they can be well separated with respect to their gamma-energies. ^{60}Co and also ^{58}Co , appearing at 0.8 MeV energy, were measured after the decay of the manganese and copper activities (Fig. 6).

As apparent from Table II paper chromatography yields adequate results for the separation of Cr, Ni, Co, Cu and Mn, while for Cd, Mo and Fe it may be considered as a suitable method for semi-quantitative analysis.

SUMMARY

A method for the determination of several impurities in reactor grade uranium compounds by post-irradiation paper chromatography is described. The bulk of the uranium is removed before irradiation by spotting the uranyl nitrate solution on to a Schleicher & Schüll 2043A paper, then chromatographing with diethyl ether containing 5 vol. % nitric acid as solvent.

The paper strip containing the contaminants which did not move away from the starting point is ashed, then irradiated. After irradiation it is dissolved and the hydrochloric acid solution chromatographed using ethyl alcohol-hydrochloric acid-water (75:20:5) as solvent. The chromatogram is then cut into sections and measured by gamma-spectrometry.

REFERENCES

- 1 W. J. FRIERSON AND J. W. JONES, *Anal. Chem.*, 23 (1951) 1447.
- 2 F. P. W. WINTERINGHAM, A. HARRISON AND R. G. BRIDGES, *Nucleonics*, 10, No. 3 (1962) 52.
- 3 D. V. COHN, G. W. BUCKALOO AND W. E. CARTER, *Nucleonics*, 13, No. 8 (1955) 48.
- 4 R. COULOMB, *Compt. Rend.*, 254 (1962) 4328.
- 5 R. COULOMB AND J. C. SCHILTZ, *Radiochem. Methods Anal., Proc. Symp., Salzburg, Austria, 1964*, Vol. II, 1965, p. 177.
- 6 M. ÖRDÖGH, D. HEGEDÜS AND E. SZABÓ, *KFKI Közlemeny*, 12 (1964) 344.
- 7 M. ÖRDÖGH, E. SZABÓ AND D. HEGEDÜS, *Radiochem. Method Anal., Proc. Symp., Salzburg, Austria, 1964*, Vol. I, 1965, p. 175.
- 8 A. TRAVESI AND J. A. GALIANO, *Radiochem. Methods Anal., Proc. Symp., Salzburg, Austria, 1964*, Vol. I, 1965, p. 153.
- 9 L. KOSTA AND G. B. COOK, *Talanta*, 12 (1965) 977.
- 10 A. SCHNEER-ERDEY, *Talanta*, 10 (1963) 591.

J. Chromatog., 25 (1966) 464-470