

treated with Aliquat-336 in the thiocyanate form and a developing solution consisting of 0.2M NH_4SCN + 0.05N H_2SO_4 (Am, R_F 0.35; Tm, R_F 0.77; Eu, R_F 0.81).

Acknowledgement

The authors are grateful to Dr. P. GERONTOPOULOS for his helpful cooperation in this work.

CAMEN, *San Piero a Grado, Pisa (Italy)*

P. G. BARBANO
L. RIGALI

1 F. L. MOORE, *Anal. Chem.*, 36 (1964) 2158.

2 P. TH. GERONTOPOULOS, L. RIGALI AND P. G. BARBANO, *Radiochimica Acta*, 4 (1965) 75.

Received January 2nd, 1967

J. Chromatog., 29 (1967) 309-311

Application of reversed-phase column chromatography to the determination of tungsten in stainless steels by activation analysis

As is well known, activation analysis is a very useful tool for the determination of trace elements in various materials, and tungsten is a normal minor component in stainless steels. However, when steel is irradiated, several other radio-isotopes besides tungsten are produced, for example, when samples are irradiated for one hour and then "cooled" for one day, the gamma-activity due to the long-lived nuclides ^{51}Cr , ^{59}Fe , ^{58}Co , ^{76}As , ^{187}W remains. As shown in Fig. 1, the resolution of gamma-spectrometry is not sufficient to resolve the complex spectrum obtained under these conditions, and therefore it is impossible to determine tungsten without previous chemical separation. On the other hand, determination of tungsten by the classical method of tungstic acid precipitation does not give a good quantitative separation because of the co-precipitation of other elements such as As, Mo, and so on¹. Better results have been obtained by isolating tungsten, as WO_4^- , on chromatographic columns of an inert support impregnated with 8-hydroxyquinoline² or on anion-exchange resins³. In this work, we have used reversed-phase partition chromatography⁴⁻⁶ to isolate tungsten from the unwanted major components of the steel.

HAMLIN *et al.*⁷ used polytrifluorochloroethylene (Kel-F) as an inert support for tri-*n*-octylamine (TNOA); this compound behaves just like a "liquid anion exchanger": the anionic metal complexes are retained on the top of the chromatographic column, while the elements which do not form anionic complexes are quickly eluted. Generally the separative properties of the column depend on the values of the complex formation constants and on the distribution coefficients between the organic and the aqueous phase. The amine extraction technique is particularly convenient because it also works efficiently in strong acid solutions.

J. Chromatog., 29 (1967) 311-315

Experimental

Equipment and reagents. The samples were irradiated in the TRIGA reactor of C.S.N. Casaccia (Rome) and examined by gamma-ray spectrometry.

The gamma-ray spectrometer consisted of an Intertechnique 400-channel pulse height analyzer with a 3×3 in. NaI (Tl) crystal mounted on a photomultiplier, Dumont 6393.

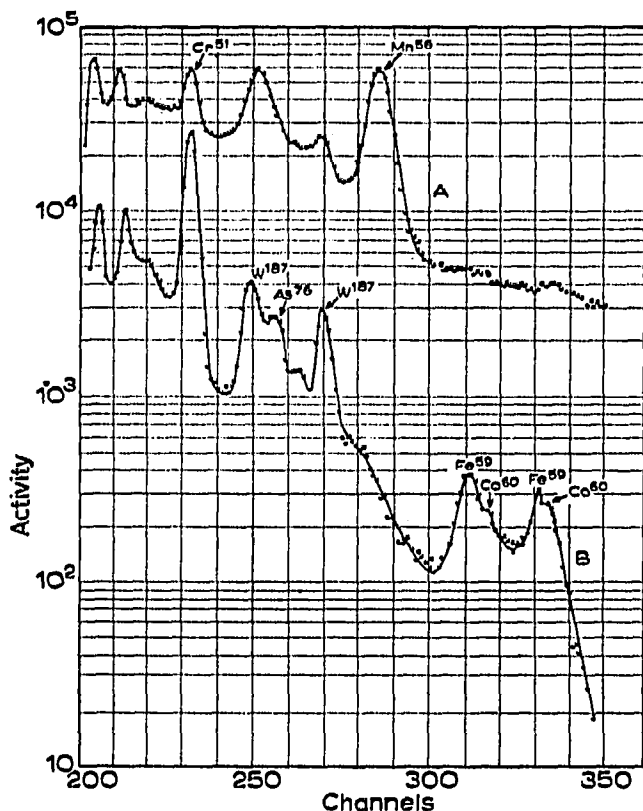


Fig. 1. Gamma-spectra of an EN 58 B sample irradiated one hour before chemical separation. (A) After 18 hours, the contribution of some nuclides at 0.5 MeV and of ^{56}Mn at 0.82 MeV overlaps the tungsten photopeak; (B) after 10 days, only ^{76}As , ^{187}W and ^{60}Co , together with a high chromium background, remain.

The columns were prepared by mixing (1:1) Kel-F moulding powder (140–200 mesh) and TNOA.

The standard solution contained 1 mg/ml of W as spectrographically pure Na_2WO_4 (Johnson & Matthey Co., London).

Preparation of the chromatographic columns. A mixture was made by adding 6 g of Kel-F to 6 ml of TNOA 50% in xylene. 20 ml of 10M HCl were then added and the suspension poured into the column. The columns, which had an internal diameter of 1 cm, and an effective length of 10 cm, were fitted with a glass disc at the bottom. Flow rate was regulated by gentle pressure from a mercury device.

Irradiation. Samples and comparative standard were irradiated in the pneumatic tube of the reactor. The flux was $1.6 \cdot 10^{12}$ n cm^{-2} sec^{-1} , and the irradiation time was one hour. The samples were rectangular pieces of stainless steel (25–30 mg). The standard consisted of 0.2–0.3 ml of the Na_2WO_4 solution contained in a polyethylene

tube sealed by heating. Samples and comparative standards were irradiated simultaneously and placed side by side in a polyethylene irradiation capsule.

Counting. Gamma-ray spectrometry was used to determine the amount of radioactivity and to ascertain the radiochemical purity of the isolated nuclides.

The eluted fractions were standardized to an equal volume in a polyethylene flask, which was accurately adjusted to the supporting ring in order to obtain identical counting geometry. Calculations were made by considering the 0.48 MeV photopeak area of ^{187}W .

Chromatographic procedure. Before irradiation each sample was cleaned by treating with concentrated hydrochloric acid and distilled water to eliminate the probable impurities. As the activity of ^{60}Co produced during the one hour of irradiation was not sufficient, this radionuclide was added as a tracer to the irradiated sample conveniently dissolved in concentrated hydrochloric acid. After evaporation to dryness the residue was dissolved with the minimum quantity of 10M HCl (2–3 ml) and the solution placed on the chromatographic column: 30 ml of 10M HCl were then added to elute Cr(III) which does not give anionic hydrochloric complexes. Cobalt moved very slowly and Fe(III) was firmly held on the top of the column. Tungsten remained on the top of the column together with Co(II) and Fe(III). After the elution of chromium, a 7M HCl–1M HF system³ was utilized to elute tungsten, which appeared immediately and was totally recovered. Cobalt was rapidly eluted with 3M HCl, and iron with 1M HNO_3 . Fig. 2 shows the elution curves for the four metal ions,

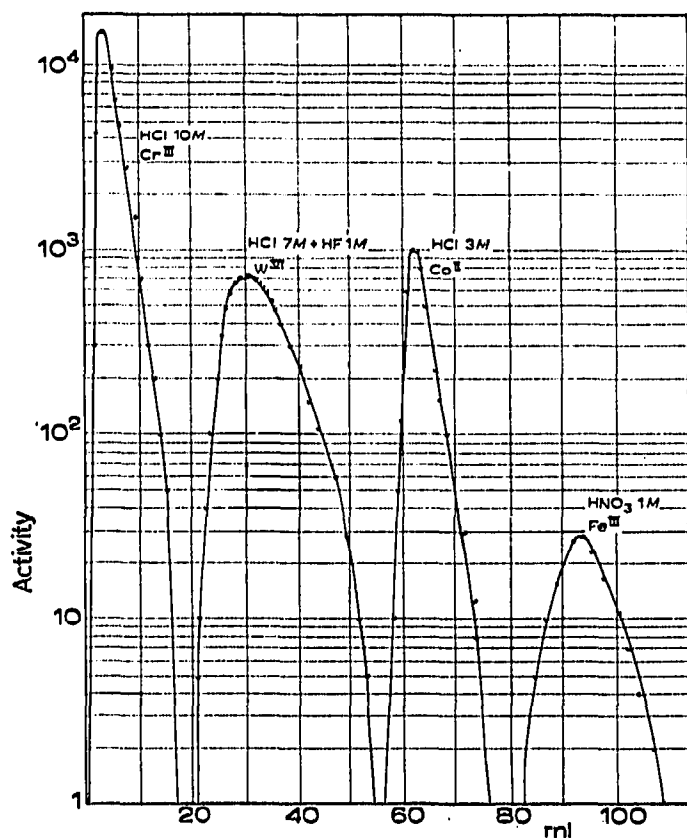


Fig. 2. Elution curves of Cr(III), W(VI), Co(II) and Fe(III) with a Kel-F-TNOA column. Length of the bed: 10 cm; volume: 9 ml; flow rate: 0.5 ml/min.

it shows that it would be also possible to use this method for the isolation of Co(II) from Fe(III) and hence for cobalt determination in the stainless steels.

Results and discussion

Some EN58B, AISI 321 and X15 UNI 1808 stainless steel samples were analyzed by means of the described technique: the results are reported in Table I,

TABLE I
TUNGSTEN CONTENTS IN 18-8 TYPE STEELS

Type	Sample No.	Weight (mg)	Tungsten (%)	Mean value (p.p.m.)	Mean error	
					(p.p.m.)	(%)
EN 58 B	1	31.0	$1.190 \cdot 10^{-1}$	1,158	± 49	4
	2	39.7	$1.087 \cdot 10^{-1}$			
	3	25.3	$1.160 \cdot 10^{-1}$			
	4	21.1	$1.195 \cdot 10^{-1}$			
AISI 321	1	26.5	$1.05 \cdot 10^{-2}$	123	± 6	5
	2	25.6	$1.20 \cdot 10^{-2}$			
	3	25.5	$1.35 \cdot 10^{-2}$			
	4	25.6	$1.30 \cdot 10^{-2}$			
UNI 1808	1	28.7	$6.4 \cdot 10^{-3}$	67.2	± 3.2	6
	2	26.2	$6.5 \cdot 10^{-3}$			
	3	22.3	$6.9 \cdot 10^{-3}$			
	4	25.1	$7.1 \cdot 10^{-3}$			

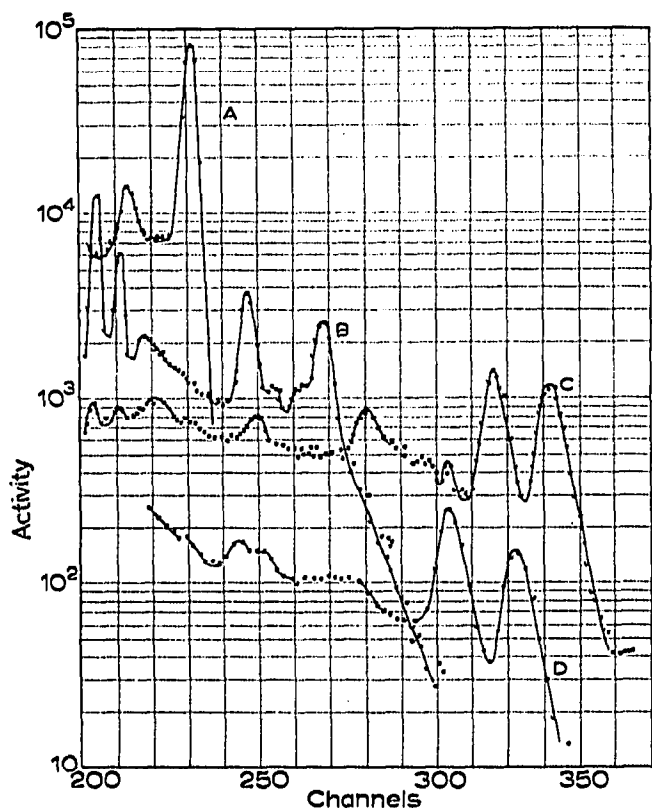


Fig. 3. Gamma-spectra of the eluted fractions: (A) chromium; (B) tungsten; (C) cobalt; (D) iron (the absence of cobalt was tested on the sum peak at 2.5 MeV).

which shows that this method is suitable both for low and medium tungsten concentrations. The relative mean error (5 % for four determinations) is a normal one for activation analysis techniques.

The tungsten fraction and the other three fractions were radiochemically pure, as shown in Fig. 3.

Kel-F-TNOA columns could be used for 10 consecutive cycles. On the basis of these results the Kel-F-TNOA columns were found suitable for the isolation and determination of tungsten, and subsequently cobalt in stainless steels. They have a great capacity and selectivity, very well defined elution curves, and give a radiochemically pure tungsten fraction. The time required for this method is about three hours including the irradiation time.

Acknowledgements

The authors gratefully thank Doctors C. TESTA, C. CESARANO and A. MOAURO for the helpful discussions throughout the course of this work. Thanks are also due to the authority of C.S.N. Casaccia of CNEN (Rome).

Laboratorio de Radioisótopos,
Facultad de Ingeniería,
Universidad de Buenos Aires (Argentina)

CARLOS E. ESPAÑOL*
AÑA MARÍA MARAFUSCHI

1 G. LELIAERT, H. HOSTE AND Z. EECKHAUT, *Talanta*, 2 (1959) 115.

2 G. ROBINSON, *Metallurgia*, 37 (1947) 45.

3 K. A. KRAUS AND F. NELSON, *Symposium on Ion Exchange and Chromatography*, ASTN Special Technical Publication No. 195, 1958.

4 B. T. KENNA, *AEC (U.S.A.) Rept.*, TID-16296 (1963).

5 E. CERRAI AND C. TESTA, *J. Chromatog.*, 6 (1961) 443.

6 E. CERRAI AND C. TESTA, *J. Chromatog.*, 9 (1962) 216.

7 A. G. HAMLIN, B. J. ROBERTS, W. LOUGHLIN AND S. G. WALKER, *Anal. Chem.*, 33 (1961) 1547.

Received December 19th, 1966

* Fellowship of the Consejo Nacional de Investigaciones Científicas de la República Argentina

J. Chromatog., 29 (1967) 311-315

Erratum

J. Chromatog., 26 (1967) 276-279

Page 278, the formula:

$$V \text{ (ml)} = \frac{(1 - E_a \times V_a)}{E_b \times V_b} \times V_p$$

should be replaced by:

$$V \text{ (ml)} = \left(1 - \frac{E_a \times V_a}{E_b \times V_b}\right) \times V_p.$$