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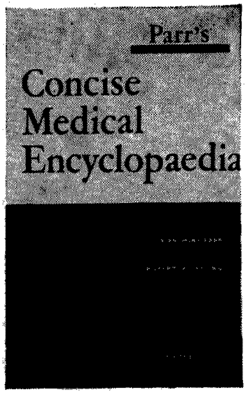
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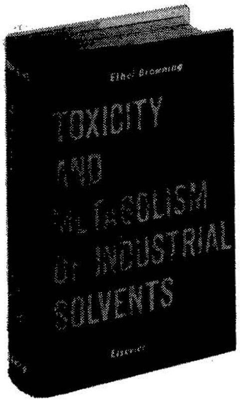
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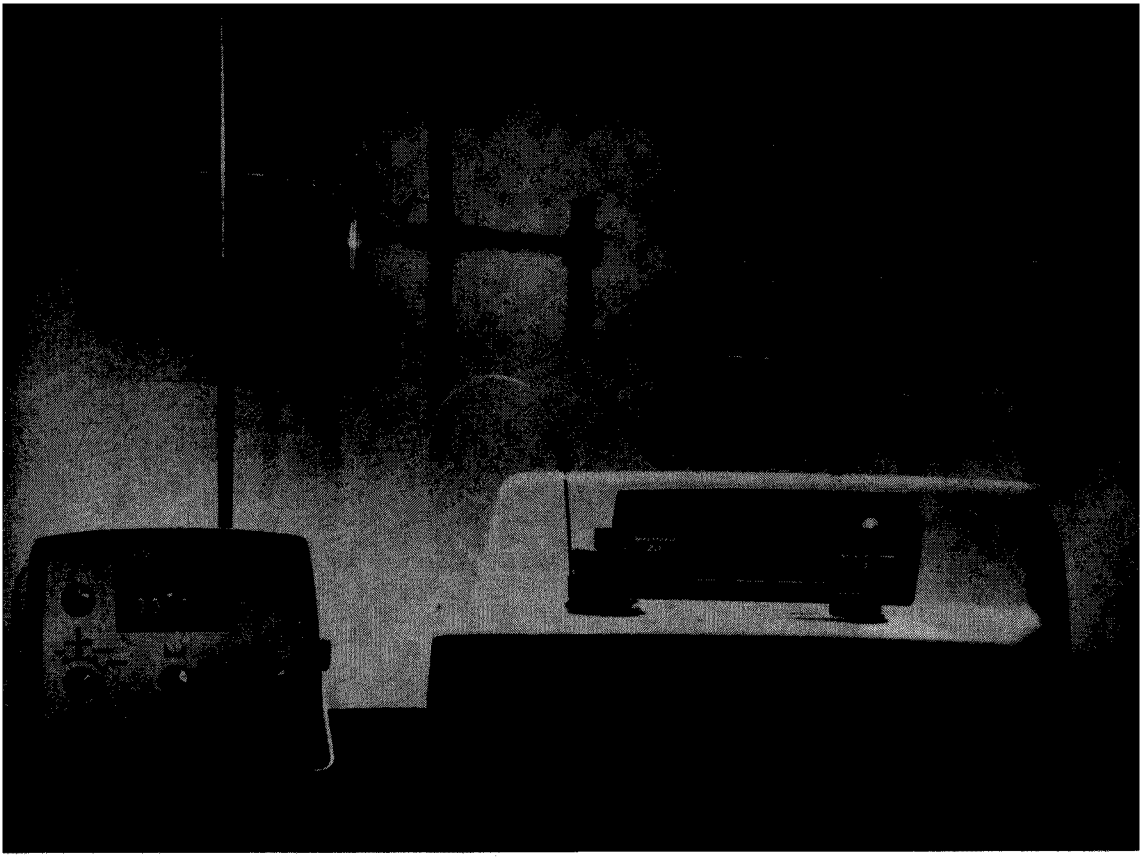

SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 34, No. 3, March 1966

DETERMINATION OF TRACE ELEMENTS IN IRON BY NEUTRON-ACTIVATION TECHNIQUES

A systematic analytical procedure for the determination of some trace impurities in iron matrices was developed by employing both direct and destructive neutron-activation techniques. Irradiations in fast neutron fluxes, selective activation by epithermal neutrons and coincidence γ-spectrometry measurements were used in some cases, in order to improve the sensitivity for non-destructive analysis; for destructive methods, radiochemical separations based on ion exchange and solvent extraction were applied. Procedures are described, and some results of the determination of low concentrations of Al, Mn, Ti, V (non-destructive), P, S, Zn (destructive) and As, Co, Cr, Cu, Mo, Ni, Sc, W (both methods) in iron are reported and discussed.

R. Malvano and P. Grosso,
Anal. Chim. Acta, 34 (1966) 253–268.

THE ATOMIC ABSORPTION SPECTROSCOPY OF LEAD

Lead can be determined by atomic absorption spectroscopy at 3 wavelengths. The relative sensitivities are 1:1.5:300. No interferences were found from the cations studied. Anionic interferences were numerous and extensive, but were removed by adding EDTA. The use of a "T"-piece increased the sensitivity of atomic absorption when flame atomizers were used. However, extreme care was necessary in controlling flame conditions both with respect to oxygen–fuel ratio and the type of solvent used. The absorption by combustion products in the flame was high, and in many cases, much greater than that of the lead itself.

The most sensitive conditions for the determination of lead appeared to be as follows: Wavelength, 2170 Å; solvent, aqueous or organic; flame, oxy–hydrogen, with the hydrogen atomizing the sample (reversed from normal). A flame adapter enabled detection limits of 0.013 p.p.m. to be reached.

C. L. Chakrabarti, J. W. Robinson and P. W. West,
Anal. Chim. Acta, 34 (1966) 269–277.

THE MICROCHEMICAL ANALYSIS OF DUST SAMPLES FOR LONG-LIVED URANIUM FISSION PRODUCTS

(in German)

A microchemical qualitative and quantitative separation process for long-lived radionuclides from uranium fission (Cs, Sr, Ce, Zr, Ru) in dust samples is described. The loaded dust filter is moistened with carrier solution and with borax–sodium carbonate, and ashed in an electrically heated platinum spiral; the dust is thus decomposed, forming beads. The solution of the bead in dilute acid is concentrated in a ring with the ring oven; the paper bearing the radioactive ring is cut into sectors and a specific precipitation reaction is applied for each nuclide in separate sectors. Identification and determination are carried out by autoradiography of the sectors. Practical testing was done with a 2.5-year old dust sample originating from nuclear studies in 1961–62; radioactive Cs, Sr and Ru were detected in 1.7 mg of dust ash. The quantitative evaluation of strontium-90 of the order of 10^{-12} C showed the sensitivity of the method. The range of application of the method is indicated.

F. Loley and H. Malissa,
Anal. Chim. Acta, 34 (1966) 278–293.

DIRECT SPECTROGRAPHIC DETERMINATION OF IMPURITIES IN URANIUM TETRAFLUORIDE

A direct spectrographic method for the determination of some impurities in UF_4 is described. The sample in the graphite electrode was covered with a layer of alumina before the arc was struck; alumina prevents the volatilization of UF_4 and thus avoids high spectral and background interferences. To stabilize the discharge, a controlled atmosphere of argon and oxygen was used. The impurity elements were divided into 3 categories according to their volatility: high (B, Si), medium (Co, Mn, V, Mo, Ti, etc.), and low (Ni, Pb, alkaline earths, etc.). Impurities of high and medium volatility could be determined with germanium or aluminum as internal standard. The sensitivities found for this method generally agreed with those of the carrier distillation method. The coefficients of variation varied from 8 to 25% at the 25 p.p.m. level.

B. PODOBNIK AND M. ŠPENKO,
Anal. Chim. Acta, 34 (1966) 294–301.

SPECTROPHOTOMETRIC DETERMINATION OF MOLYBDENUM IN STEEL, TANTALUM, NIOBIUM OR TUNGSTEN

A rapid, accurate spectrophotometric method for the determination of 0.001–0.1% of molybdenum in steel, tantalum, niobium or tungsten is presented. The molybdenum is isolated, when required, by solvent extraction with α-benzoinoxime–chloroform solution or cupferron–chloroform solution and then determined by the thiocyanate method. Conditions for obtaining high sensitivity by quantitative reduction of molybdenum(VI) to molybdenum(V) with tin(II) chloride have been established. It has been shown that fading of the molybdenum(V)-thiocyanate color can be minimized by adding hydroquinone to prevent air oxidation of molybdenum(V).

C. L. LUKE,
Anal. Chim. Acta, 34 (1966) 302–307.

SEPARATION OF LARGE AMOUNTS OF IRON(III) FROM COBALT, NICKEL, AND ALUMINIUM BY COMBINED ION EXCHANGE–SOLVENT EXTRACTION

A method is described for the cation-exchange separation of large amounts of iron(III) from cobalt, nickel, and aluminium. On the strongly acidic Dowex 50-X8, iron(III) is not adsorbed from an 80% tetrahydrofuran–20% 3 *M* hydrochloric acid mixture, while cobalt, nickel, and aluminium are retained; a quantitative separation is thus possible. Cobalt and nickel or aluminium are then separated by elution with 90% tetrahydrofuran–10% 6 *M* hydrochloric acid. In these mixtures combined ion exchange–solvent extraction appears to occur; both ion exchange and liquid–liquid extraction are effective simultaneously.

J. KORKISCH AND S. S. AHLUWALIA,
Anal. Chim. Acta, 34 (1966) 308–313.

DETERMINATION OF ALUMINUM AND IRON BY SOLVENT EXTRACTION AND GAS CHROMATOGRAPHY

A method which combines solvent extraction and gas chromatography for the determination of aluminum and iron in the same sample is given. The two metals are extracted into benzene with trifluoroacetylacetone and a portion of the benzene layer was injected into a gas chromatograph. The two chelates gave well resolved symmetrical peaks. The method was tested by analyzing a National Bureau of Standards alloy, number 162A. Copper and nickel, which would normally interfere when present in large amounts, were masked with picolinic acid. In addition a solvent extraction separation of iron from aluminum and a spectrophotometric determination of iron is described.

G. P. Morie and T. R. Sweet,
Anal. Chim. Acta, 34 (1966) 314–321.

IDENTIFICATION AND DETERMINATION OF PHENOLS AND CHLOROPHENOLS IN VERY DILUTE AQUEOUS SOLUTIONS BY GAS–LIQUID CHROMATOGRAPHY, PAPER CHROMATOGRAPHY AND SPECTROPHOTOMETRY

After concentration of the organic substances from water samples of 700 to 20,000 l by adsorption on active carbon and desorption with chloroform in a large Soxhlet apparatus, the organic compounds were separated by extraction into 5 different groups: acids, phenols, bases, neutral and amphoteric substances. The phenol group was investigated by gas and paper chromatography, ultraviolet difference spectrophotometry and infrared spectroscopy. Phenol, 2,4,6-trichlorophenol, 2- and 3-cresol, 2,4-xylenol and 2,4-dichlorophenol were identified in samples of raw and treated water. Quantitative measurements proved to be possible with gas chromatography. The conditions for quantitative desorption and separation were studied.

S. Goren-Strul, H. F. W. Kleijn and A. E. Mostaert,
Anal. Chim. Acta, 34 (1966) 322–336.

THE DETERMINATION OF VANADIUM IN SEA AND NATURAL WATERS, BIOLOGICAL MATERIALS AND SILICATE SEDIMENTS AND ROCKS

Vanadium was concentrated from sea and natural waters by coprecipitation with iron(III) hydroxide, and separated from iron and other elements by ion exchange, using hydrogen peroxide as a very selective eluting agent. The element was determined photometrically with diaminobenzidine. The ion-exchange process was also used to separate vanadium from other elements in the analysis of silicate rocks and marine plants. Coefficients of variation of 2.8%, 1.3% and 2.5% were found for the determination of the element in sea water, marine sediments and marine plants at levels of 1.8 μg/l, 57 μg/g and 2.2 μg/g, respectively. The U.S. Geological Survey standard granite G1 was found to contain $17.2 \pm 0.9\ \mu$g V/g.

K. M. Chan and J. P. Riley,
Anal. Chim. Acta, 34 (1966) 337–345.

THE DETERMINATION OF MICRO AND SUBMICRO TRACES OF MANGANESE BY ANODIC STRIPPING POLAROGRAPHY

(in French)

A method is proposed for the determination of manganese(II) by anodic stripping polarography. A systematic study was made of the various factors affecting the course of pre-electrolysis as well as the anodic stripping. A procedure is given for the determination of 1 ng of manganese with a precision of $\pm 12.7\%$. The selectivity of the method was studied in the presence of 14 cations; hydrogen ions interfere at pH < 5, Co^{2+} interferes at concentrations equal to that of Mn^{2+}, and Mo^{7+} and V^{5+} at concentrations $\geqslant 50$ times that of Mn^{2+}. The other ions studied do not interfere at concentrations 100–1000 times higher. An application to pharmaceutical analysis is described.

D. Monnier, E. Martin and W. Haerdi,
Anal. Chim. Acta, 34 (1966) 346–359.

A RAPID METHOD FOR THE DETERMINATION OF ORGANIC NITROGEN AND PHOSPHORUS BASED ON A SINGLE PERCHLORIC ACID DIGESTION

Results of nitrogen determinations obtained by perchloric acid digestion of organic matter under reflux were found to be equivalent to those obtained by the conventional sulfuric acid Kjeldahl method. A rapid determination of nitrogen and phosphorus was thus possible after a single perchloric acid digestion. Nitrogen was determined by nesslerization and phosphorus by a conventional molybdenum blue technique. The method devised was found satisfactory for a great variety of natural products and pure organic compounds, including materials containing all kinds of tertiary nitrogen.

D. S. Galanos and V. M. Kapoulas,
Anal. Chim. Acta, 34 (1966) 360–366.

DETERMINATION OF AMERICIUM AND RARE EARTHS BY GRAVIMETRIC MICROANALYSIS

(Short Communication, in French)

F. Clanet and M. Pagès,
Anal. Chim. Acta, 34 (1966) 367–369.

A RAPID METHOD FOR THE SIMULTANEOUS DETERMINATION OF TOTAL CARBON AND CARBON-14 IN SMALL SAMPLES

(Short Communication)

J. D. van der Laarse and H. C. E. van Leuven,
Anal. Chim. Acta., 34 (1966) 370–371.

THE DETERMINATION OF GOLD IN COSMIC DUST COLLECTION BY NUCLEAR ACTIVATION ANALYSIS

(Short Communication)

T. K. Choy,
Anal. Chim. Acta, 34 (1966) 372–374.

DETERMINATION OF MANGANESE(II) IN MANGANESE SALTS OF HIGHER OXIDATION STATE BY ELECTRON SPIN RESONANCE

(Short Communication)

E. G. Janzen and M. Agerton,
Anal. Chim. Acta, 34 (1966) 374–375.

DETERMINATION OF TRACE ELEMENTS IN IRON BY NEUTRON-ACTIVATION TECHNIQUES[*]

R. MALVANO AND P. GROSSO
SORIN, Centro Ricerche Nucleari, Saluggia (Italy)

(Received June 23rd, 1965)

Neutron-activation techniques have been widely employed for analysis of ferrous materials at trace levels[1,2] and at higher concentrations[3–5].

A systematic analysis scheme suitable for routine work was developed in the SORIN laboratories, and conditions as far as possible favourable to non-destructive measurements in a wide range of impurity concentrations were studied. The method was applied to the determination of such elements as Al, As, Co, Cr, Cu, Mn, Mo, Ni, P, Sc, Ti, V, W and Zn in pure iron samples. Tests on commercially available pure iron samples and on synthetic samples, prepared by adding known amounts of elements to high purity iron, were performed by irradiating in different positions of the RS1 pool-reactor and using both direct and destructive techniques.

TABLE I

NUCLEAR CHARACTERISTICS OF Fe AND STUDIED IMPURITIES

Element	*Target nuclide*	*Isotopic abundance (%)*	*Nuclear reaction*	*Cross-section[a] (barns)*	*Produced radionuclide*	*Half-life*	*Measured emission and energy (MeV)*
Fe	^{58}Fe	0.31	(n,γ)	0.98	^{59}Fe	45.1 d	γ; 1.10, 1.29
Al	^{27}Al	100	(n,γ)	0.23	^{28}Al	2.3 m	γ; 1.78
As	^{75}As	100	(n,γ)	4.2	^{76}As	26.6 h	γ; 0.56
Co	^{59}Co	100	(n,γ)	20 38	^{60m}Co ^{60}Co	10.5 m 5.27 y	γ; 0.059 γ; 1.17, 1.33
Cr	^{50}Cr	4.3	(n,γ)	15	^{51}Cr	27.8 d	γ; 0.32
Cu	^{63}Cu	69.1	(n,γ)	4.1	^{64}Cu	12.8 h	γ; 0.51($\beta +$ annih.)
Mn	^{55}Mn	100	(n,γ)	13.3	^{56}Mn	2.58 h	γ; 0.85
Mo	^{98}Mo	23.7	(n,γ)	0.45	^{99}Mo + ^{99m}Tc	67.0 h	γ; 0.14
Ni	^{58}Ni	67.8	(n,p)	0.10[b]	^{58}Co	72 d	γ; 0.51 ($\beta +$ annih.), 0.81
P	^{31}P	100	(n,γ)	0.21	^{32}P	14.3 d	β; 1.71
S	^{32}S	95.0	(n,p)	0.065[b]			
Sc	^{45}Sc	100	(n,γ)	22	^{46}Sc	85 d	γ; 0.89, 1.12
Ti	^{46}Ti	8.0	(n,p)	0.012[b]			
V	^{51}V	99.8	(n,γ)	5.1	^{52}V	3.77 m	γ; 1.44
W	^{186}W	28.4	(n,γ)	34	^{187}W	24.0 h	γ; 0.072, 0.135
Zn	^{64}Zn	48.9	(n,γ)	0.40	^{65}Zn	245 d	γ; 1.11

[a] For thermal neutrons except when otherwise indicated.
[b] For a fission spectrum.

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[*] Work performed under Euratom Contract No. 004-63-10 TEEI.

In Table I the nuclear characteristics of the elements taken into account are reported.

DIRECT ACTIVATION ANALYSIS

Non-destructive techniques, based on γ-spectrometry, are sometimes preferred in order to save time, and are essential when further assays must be performed on individual samples.

The choice of proper irradiation and decay periods can limit the produced activities to a few species which are easily measured; in the case of iron analysis, the radioactivity arising from the matrix itself (short-lived ^{56}Mn, long-lived ^{59}Fe and ^{54}Mn) and from common impurities, sets a limit to the feasibility of non-destructive determinations.

Direct methods of analysis were studied for 10 impurities in iron samples by improving the sensitivity with the aid of special irradiation and counting procedures, whenever necessary.

Irradiation in fast neutrons. Some elements, such as nickel and titanium, are advantageously determined by using respectively the ^{58}Co and ^{46}Sc nuclides, produced by (n,p) reactions; the activation can be made more selective when thermal neutrons are shielded out, *e.g.* by means of a cadmium cover.

TABLE II

SPURIOUS CONTRIBUTIONS FROM COMPETITIVE REACTIONS ON Fe MATRICES IN Mn AND Cr DETERMINATIONS

Sought elements	*Interfering reactions*	*Simulated concentrations of sought element (p.p.m.)*		
		Rabbit	*Core center*	*Core surrounding*
Mn	^{56}Fe (n,p) ^{56}Mn	11.5	26	12
Cr	^{54}Fe (n,α) ^{51}Cr	12	28	13

TABLE III

Cd RATIO VALUES FOR THE ELEMENTS UNDER STUDY

(Experimental conditions: irradiations in rabbit; Fe target 400 mg/cm^2 thickness, other element 0.05 to 0.5 mg/cm^2 thickness (solutions evaporated on filter paper disks). Precision: generally within 10%, as evaluated by duplicate experiments)

Element	*Measured nuclide*	R_{Cd}	*Element*	*Measured nuclide*	R_{Cd}
Fe	^{59}Fe	45	Mo	^{99}Mo	2.2
Al	^{28}Al	40		^{101}Mo	19
As	^{76}As	4.9	Ni	^{65}Ni	90
Co	^{60m}Co	36	Sc	^{46m}Sc	105
	^{60}Co	40		^{46}Sc	99
Cr	^{51}Cr	130	Ti	^{51}Ti	52
Cu	^{64}Cu	55	V	^{52}V	94
	^{66}Cu	68	W	^{187}W	6.5
			Zn	^{65}Zn	26
Mn	^{56}Mn	56		^{69m}Zn	18

Duplicate irradiation in thermal and fast neutrons. When manganese and chromium are to be determined, the spurious contributions to the ^{56}Mn and ^{51}Cr activities due to the matrix (see Table II), are evaluated and subtracted by irradiating pure iron samples with thermal shields (Cd cover).

Irradiation in epithermal neutrons. The nuclides showing high resonance integrals may be selectively activated by shielding the thermal neutrons, *e.g.* by means of Cd covers (see Table III for some Cd ratio values, as experimentally determined in an irradiation position): the method can be utilized in order to improve the sensitivity for direct measurements of some elements in iron (As, Mo, W).

Coincidence γ-spectrometry. The radionuclides with significant emission of cascade γ-rays or positron annihilation γ-rays may be selectively measured by employing a coincidence counting device: the possibility of non-destructive determination of Cu, Ni, Co, Sc and Ti in iron is remarkably increased by coincidence measurements of ^{64}Cu and ^{58}Co (0.511-MeV annihilation γ-rays), ^{60}Co (1.17–1.33 MeV emission, about $8 \cdot 10^{-12}$ sec delay coincidence), and ^{46}Sc (0.89–1.12 MeV emission, about $7 \cdot 10^{-12}$ sec delay coincidence).

The main subdivision in analytical groups is based on the difference in half-life values for the measurable radionuclides.

Short irradiations

Some elements (Al, V, Co, Mn) can be determined by means of very short irradiations (10–30 sec) in the pneumatic irradiation facility, and by minimum decay times (usually less than 1.5 min); when standards and samples must be singly irradiated, flux monitors are employed to account for possible flux drifts.

Aluminium and vanadium. Since the 1.80-MeV peak of ^{56}Mn (impurity and spurious Fe contribution) interferes with the measurement of the 1.78-MeV activity of ^{28}Al, and the Compton background of both ^{56}Mn and ^{28}Al interferes with ^{52}V measurements at 1.43 MeV, the activities are evaluated by means of a resolution of the decay curves: a faster procedure is possible by evaluating the contribution of each activity by comparison with standard ^{56}Mn and ^{28}Al spectra. Since the ^{56}Mn activity is much longer-lived, it may be automatically separated[6] by subtracting the count after a short decay period from a spectrum previously stored in the magnetic memory of the analyzer. In this way (with standardized conditions, selected as 10-sec irradiation in rabbit, 30-sec counting time, subtraction of the count at 4-min decay time from the count at 1-min decay time) the actual sensitivity is evaluated as 1 p.p.m. Al and 0.05 p.p.m. V in Mn-free iron samples; a 100-fold amount of aluminium does not appreciably affect the vanadium analysis. In Table IV some results of aluminium and vanadium determinations in iron samples are reported.

Cobalt. Cobalt may be determined through the measurements of its short-lived nuclide ^{60m}Co; a thin scintillation detector is used to reduce the Compton background, mainly due to the ^{56}Mn activity, under the 59-keV photopeak of ^{60m}Co. The sensitivity is evaluated as 0.2 p.p.m. Co in Mn-free iron for the adopted experimental conditions (10-sec irradiation in rabbit, 60-sec decay and 30-sec counting time). The use of epithermal neutron irradiations scarcely improves the sensitivity (see Table III for Cd ratios): when Mn-rich samples are to be analyzed (Mn to Co weight ratios higher than 100), other techniques are more useful.

Special care must be taken on account of the low-energy γ-emission of ^{60m}Co:

TABLE IV

DETERMINATION OF Al AND V IN IRON SAMPLES

Sample	*Concentration (p.p.m.)*			
	Present[a]		*Found*	
	Al	*V*	*Al*	*V*
Synthetic	35.0	0.50	34.2	0.6
Synthetic	25.0	2.5	25.0	2.4
Synthetic	12.5	1.0	13.8	1.1
Synthetic	5.0	0.5	6.6	0.4
Synthetic	2.5	0.2	3.6	0.2
Armco, 99.9	—	—	25.7 ± 2.9	0.41 ± 0.08
BCS 149/1, 99.95	—	<10	$\leqslant 3$	$\leqslant 0.3$
Johnson–Matthey, 99.999	2	—	3.0 ± 0.5	0.10 ± 0.02

[a] Known amounts of elements added to high purity Fe for synthetic samples (90 to 180 p.p.m. Mn are also added), or certified values when available.

TABLE V

DETERMINATION OF Co IN IRON SAMPLES

Sample	*Co concentration (p.p.m.)*			
	Present[a]	*Found*		
		^{60m}*Co direct measurement*	^{60}*Co direct coincidence measurement*	^{60}*Co destructive measurement*
Armco, 99.9	—	48.5 ± 1.8	45 ± 10	48.2 ± 0.4
BCS 149/1, 99.95	90 ± 8	88.3 ± 2.9	118 ± 25	87.1 ± 1.1
Johnson–Matthey, 99.999	—	$\leqslant 1$	$\leqslant 5$	0.45 ± 0.05
Synthetic	$3.7 \cdot 10^3$	—	$3.8 \cdot 10^3$	—
	$5.3 \cdot 10^2$	—	$5.1 \cdot 10^2$	—
	$3.7 \cdot 10^2$	—	$3.7 \cdot 10^2$	—
	$2.7 \cdot 10^2$	—	$2.9 \cdot 10^2$	—

[a] Known amounts of Co added to high purity Fe for synthetic samples, or certified values when available.

standard and sample are counted in the same form and geometrical conditions, or corrections for self-absorption are made. In Table V some results of cobalt determination by means of different methods are reported for comparison.

Manganese. Although the main activity in short-irradiated iron samples is due to ^{56}Mn, a serious limitation for manganese determination is set by the spurious contribution from the iron matrix (see Table II); duplicate irradiations of bare and Cd-shielded samples under the same conditions allow determinations of as low concentrations of manganese as 1 p.p.m. For lower contents, a preliminary manganese separation and a subsequent activation must be envisaged, or irradiation in the well thermalized neutron flux of the reactor thermal column must be carried out. Some results for determinations of manganese are reported in Table VI.

Intermediate irradiations

Irradiation for 1 h in the central reactor position and a 10–40-h cooling time

TABLE VI

DETERMINATION OF Mn IN IRON SAMPLES

Sample	*Concentration (p.p.m.)*		
	Present[a]	*Found*	
		Duplicate irradiation (bare and Cd-shielded)	*Irradiation in thermal column*
Armco, 99.9	—	276 ± 6	—
BCS 149/1, 99.95	260 ± 2	265 ± 5	260 ± 10
Johnson–Matthey, 99.999	3	7.47 ± 0.62	7.0 ± 0.5

[a] Certified values.

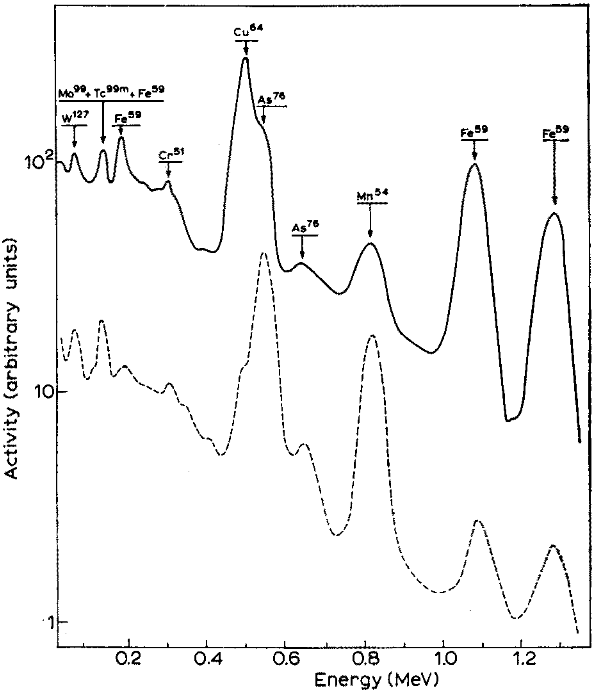

Fig. 1. γ-Spectra of short-irradiated Fe sample (Armco sample). ——, bare irradiated; – – –, Cd-shielded irradiated.

are the conditions selected for the determinations of such elements as As, Cu, Mo, and W producing radionuclides with half-lives ranging from 13 to 70 h: moreover the long-lived ^{51}Cr activity can be measured for determinations of chromium. More prolonged irradiation periods could increase the absolute sensitivity for these elements, but the actual sensitivity for non-destructive method is lowered by the long-lived activities from the iron matrix. Duplicate irradiations of bare and Cd-covered samples in flux-equivalent positions are performed to increase the concentration range of applicability of non-destructive analysis for As, Mo, W and Cr. In Fig. 1 the γ-spectra of a sample irradiated under both conditions are shown.

Arsenic and copper. Because of the small difference of the energies of the main

γ-emission of ^{76}As and ^{64}Cu, an activity resolution can be difficult, and decay measurements are time-consuming. Two methods were therefore envisaged for a fast and easy determination.

(*i*) Coincidence counting at 0.51 MeV. The ^{64}Cu annihilation emission is resolved by coincidence counting, and the ^{64}Cu contribution to the total composite peak is evaluated by measuring under both conditions a copper standard. Spurious coincidence counting from the ^{76}As activity is taken into account, whenever necessary, by similar measurement of an As standard.

(*ii*) Duplicate irradiation of bare and Cd-covered samples. Since the Cd ratio for arsenic is considerably higher than for copper (see Table III), selective arsenic activations in Cd-shielded samples are possible. The arsenic and copper concentrations can be calculated by measuring the composite peak of both samples, from the relationships

$$A = m\,\mathrm{As} + n\,\mathrm{Cu} \qquad (1)$$

$$A' = m'\mathrm{As} + n'\mathrm{Cu}$$

where A and A' are the specific activities of the composite peak, respectively of the bare and Cd-shielded samples, As and Cu the sought concentrations, and m and m', n and n' the specific activities of As and Cu as respectively measured in bare and Cd-shielded standards.

The first method is faster, and is especially useful in the case of a high As: Cu concentration ratio, while the second method is to be preferred in the opposite case. By combining the two techniques, accurate determinations in the range of As: Cu weight ratio from 60 to $7 \cdot 10^{-2}$ are possible, for the selected experimental conditions. Some results are reported in Table VII.

Molybdenum and tungsten. Irradiations in epithermal neutrons are preferred in order to reduce the activity background under the low-energy photopeaks of ^{99}Mo + ^{99m}Tc and ^{187}W (see Fig. 1): both molybdenum and tungsten, in fact, exhibit low Cd ratio values, compared with iron (see Table III). This technique is especially

TABLE VII

DETERMINATION OF Cu AND As IN IRON SAMPLES

	Concentration (p.p.m.)							
	Present[a]		*Found*					
			Duplicate irradiation (bare and Cd-covered)[b]		*Total and coincidence counting*[b]		*Destructive method*	
	As	*Cu*	*As*	*Cu*	*As*	*Cu*	*As*	*Cu*
Armco, 99.9	—	—	78.1 ± 9.1	349 ± 12	80.8 ± 4.8	342 ± 6	83.8 ± 3.5	322 ± 11
BCS 149/1, 99.95	—	< 10	6.8 ± 2.0	5.0 ± 1.8	7.4 ± 2.8	4.85 ± 0.95	5.80 ± 1.95	5.46 ± 1.01
Johnson–Matthey, 99.999	—	< 1	—	—	≤ 0.2	0.80 ± 0.12	0.062 ± 0.020	0.55 ± 0.10

[a] Certified values.

[b] Direct measurement.

useful for a simple resolution of the 0.14-MeV peak of ^{99}Mo + ^{99m}Tc from the ^{59}Fe peak at the same energy (the method was employed by BRUNE AND JIRLOW, for higher molybdenum contents[7]).

In this way the 20-p.p.m. value for direct determinations of molybdenum in iron can be reduced to about 2 p.p.m., for the adopted set of experimental conditions; corrections are made by comparing the ratio of the 0.14-MeV activity with the 0.19, 1.10 and 1.29-MeV peak of a pure ^{59}Fe standard source. A 24-h waiting time is necessary to allow the equilibrium value of the daughter ^{99m}Tc activity to be reached: moreover, when tungsten is present, the interference of the 0.135-MeV peak of ^{187}W can be reduced by means of a longer cooling period. For the experimental conditions used with a 70-h decay and with a correction by comparison of a ^{187}W standard spectrum, a 5-fold amount of tungsten was found not to interfere seriously with molybdenum determinations. In Table VIII the results for direct determinations of molybdenum and tungsten in iron samples are compared with a destructive analysis.

Chromium. Long-lived ^{51}Cr can be directly measured in iron samples, when the

TABLE VIII

DETERMINATION OF Mo AND W IN IRON SAMPLES

Sample	*Concentration (p.p.m.)*					
	Present[a]		*Found*			
			Non-destructive method		*Destructive method*	
	Mo	*W*	*Mo*	*W*	*Mo*	*W*
Armco, 99.9	—	—	48 ± 10	2.8 ± 0.4	52.0 ± 7.5	2.47 ± 0.15
BCS 149/1, 99.95	10 ± 4	—	7.5 ± 2.0	0.57 ± 0.20	8.52 ± 1.50	0.60 ± 0.05
Johnson–Matthey, 99.999	—	—	⩽ 2	⩽ 0.3	0.57 ± 0.12	0.23 ± 0.10
Synthetic	105	—	96	—	—	—
Synthetic	45	—	48	—	—	—
Synthetic	18	—	21	—	—	—
Synthetic	9	—	13	—	—	—
Synthetic	30	2.7	30	2.9	—	—
Synthetic	30	30	26	30	—	—

[a] Known amounts of elements added to high purity Fe for synthetic samples, or certified values when available.

TABLE IX

DETERMINATION OF Cr IN IRON SAMPLES

Sample	*Cr concentration (p.p.m.)*		
	Present[a]	*Non-destructive method*	*Destructive method*
Armco, 99.9	85 ± 15	60 ± 10	78.4 ± 8.4
BCS 149/1, 99.5	< 10	⩽ 15	7.4 ± 1.0
Johnson–Matthey, 99.999	—	⩽ 10	⩽ 1

[a] Certified values, or data obtained by independent methods (spectrophotometry).

activity background is reduced by short irradiations and long cooling times (1–1.5 h and 10–20 days respectively): under these conditions, the build-up of long-lived activities is low and the shorter-lived activities have decayed to negligible levels. The competitive reaction on the iron matrix simulates chromium concentrations (see Table III) that must be evaluated by irradiating a Cd-covered pure iron sample under the same conditions as the material under analysis. In Table IX the results of direct determinations are compared with more accurate destructive methods.

Long irradiations

The possibility of direct determinations of Co, Ni, Sc and Ti in iron samples was investigated for 4–5-day irradiation periods in a position around the reactor core, and decay times as long as 10–20 days. Longer irradiations and decays could result in higher sensitivity, but the tested conditions are sufficient for a satisfactory impurity level, at least for Co, Ni and Sc traces. In order to obtain more selective irradiation conditions for nickel and titanium, some Cd-shielded samples were irradiated;

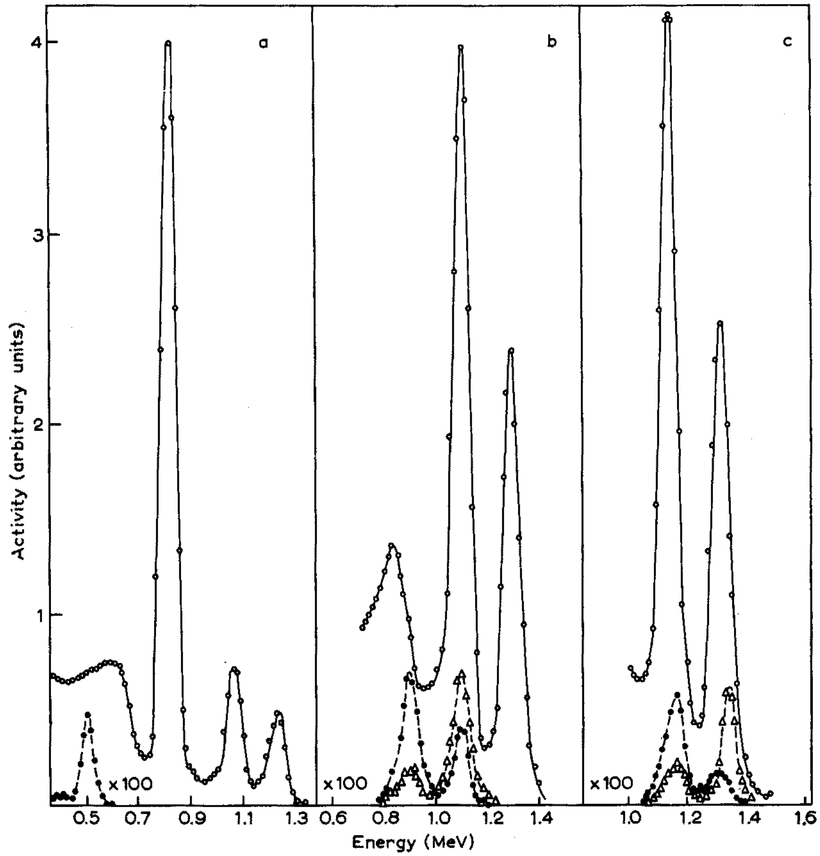

Fig. 2. Determination of Ni, Sc and Co in iron samples by means of γ-coincidence measurements. Total γ-spectrum, ○. (a) Ni determination (0.01% Ni), (Armco), coincidence at 0.51 MeV ●; (b) Sc determination (2.5 p.p.m. Sc), (Fe synthetic samples), coincidence at 0.89 MeV ▲, coincidence at 1.12 MeV ●; (c) Co determination (0.01% Co), (BCS 149/1), coincidence at 1.17 MeV ▲, coincidence at 1.33 MeV ●.

coincidence γ-spectrometry was used in order to resolve the activity to be measured from the prevailing ^{59}Fe activity[8,9] (see Fig. 2); corrections for spurious coincidence from ^{59}Fe must be made for lower impurity concentrations, by counting pure ^{59}Fe sources.

Nickel. The ^{58}Co activity is resolved by coincidence counting at 0.51 MeV; for the employed experimental conditions, 60 p.p.m. was found to be the limiting value in unshielded samples, and 5 p.p.m. in Cd-shielded samples.

Cobalt. By measuring the coincidence at 1.17 or 1.33 MeV, the ^{60}Co activity is selectively measured; cobalt concentrations as low as 5 p.p.m. represent the limit of sensitivity for the selected conditions. This method is especially useful for Mn-rich iron samples for which the direct measurement of ^{60m}Co is difficult.

Scandium and titanium. Both elements are measured through the ^{46}Sc activity by coincidence counting at 0.89 or 1.12 MeV, but scandium can be determined far more sensitively by activation analysis. The sensitivity for scandium is 0.1 p.p.m. for the experimental conditions used, while for titanium the limit is about 500 p.p.m. In the case of a Ti:Sc concentration ratio higher than $2 \cdot 10^3$, corrections must be made

TABLE X

DETERMINATION OF Ni IN IRON SAMPLES

Sample	*Ni concentration (p.p.m.)*		
	Present[a]	*Found*	
		Non-destructive method (Cd-covered irradiated samples, coincidence counting)	*Destructive method*
Armco, 99.9	—	129 ± 19	110 ± 13
BCS 149/1, 99.95	20 ± 2	35 ± 10	22.1 ± 1.2
Johnson–Matthey, 99.999	2	$\leqslant 5$	1.40 ± 0.14
Synthetic	$3.6 \cdot 10^3$	$3.6 \cdot 10^3$	—
	$3.6 \cdot 10^2$	$4.0 \cdot 10^2$	—

[a] Known amounts of Ni added to high purity Fe for synthetic samples or certified data when available.

TABLE XI

DETERMINATION OF Sc AND Ti IN IRON SAMPLES

Sample	*Concentration (p.p.m.)*			
	Present[a]		*Found*	
	Sc	*Ti*	*Sc*	*Ti*
Synthetic	10	—	10	—
Synthetic	6.2	—	6.0	—
Synthetic	2.5	—	2.2	—
Synthetic	—	$2.5 \cdot 10^4$	—	$2.55 \cdot 10^4$
Synthetic	—	$1.6 \cdot 10^4$	—	$1.56 \cdot 10^4$
Synthetic	—	$5.2 \cdot 10^3$	—	$5.8 \cdot 10^3$

[a] Known amounts of elements added to high purity Fe.

for the determination of scandium and both elements can be determined by a duplicate irradiation and applying a relationship like (1).

In Tables V, X and XI, some analytical results are reported.

DESTRUCTIVE ACTIVATION ANALYSIS

A radiochemical separation of the activities is generally required when pure β-emitters, like ^{32}P, are to be measured; furthermore, higher precision and analytical sensitivity are usually reached when separated single activities can be measured.

The chemical separation of some activity groups was developed, and iron samples were analyzed by using these techniques. A method of destructive analysis for aluminium and vanadium was not taken into consideration, as special fast radiochemical procedures must be envisaged for short-lived ^{28}Al and ^{52}V; in any case, the sensitivity level of the non-destructive method can be considered as satisfactory in most cases. Similarly, special procedures for the preliminary separation of manganese and chromium traces from the iron matrix were not studied, so that the minimum detectable concentration of these elements is fixed by the spurious contributions from iron.

Chemical separations for two activity groups, based on the half-life characteristics, were developed, by utilizing simple techniques suitable for a routine procedure, such as ion exchange (studied on the basis of the work reported by KRAUS AND NELSON[10]), and solvent extraction.

Short-lived activity group

With 1–5-h irradiation and 10–30-h decay times, the main activities in the sample are those arising from Cu, As, Mo and W impurities and from the matrix itself: ^{64}Cu, ^{76}As, ^{99}Mo, ^{187}W, ^{59}Fe, ^{54}Mn.

TABLE XII

REMOVAL OF IRON BY ISOPROPYL ETHER EXTRACTION[a]

Element	*% Recovery in aqueous solution*	*Element*	*% Recovery in aqueous solution*
Fe	0.10±0.05	Mo	82.5±3.5
As	99.9±0.1	P	99.9±0.2
Co	101±1	Sc	101±0
Cr	100±1	W	99.1±1.0
Cu	99.1±1.1	Zn	80.5±1.5
Mn	99.8±0.5		

[a] Experimental conditions: 0.3 g Fe, ~ 10 µg W and 1 mg of each other element used as carrier in 20 ml of 9 *N* HCl solution; continuous extraction with 40 ml of ether for 45 min.

A preliminary removal of the bulk of iron by an isopropyl ether extraction (see Table XII), and a subsequent separation by anion exchange as illustrated in Table XIII, can form the basis of a procedure, although molybdenum is partially co-extracted with iron, and the manganese activity (which generally does not interfere) is collected with the arsenic fraction. A faster technique which does not require any preliminary elimination of the matrix was developed: after a previous reduction, iron is washed out of the resin column, by operating in a nitrogen atmosphere in order to prevent a possible re-oxidation of iron(II) on the resin. Arsenic, copper and tungsten +molybdenum are separated as indicated in Table XIV. No further separation of tungsten and molybdenum is generally necessary, as in most instances the ^{187}W interference on the ^{99}Mo+^{99m}Tc peak is easily corrected; these elements could be separated from each other, if required, by utilizing some of the techniques reported in the literature[11,12]. The arsenic and copper elution fractions are directly counted, and the molybdenum and tungsten activities are measured on the resin: corrections are needed to account for the different geometry of comparison standards by means of a correction factor previously calculated by comparing the same activity of sources in the different forms. Previous tracer tests confirmed that for the adopted single-step procedure the recovery is quantitative, and therefore no inactive carrier is added and chemical yields are not checked in routine experiments.

In Tables VII and VIII the results of destructive determinations of As, Cu, Mo and W are compared with those obtained from direct measurements.

Long-lived activity group

After irradiations of about 100 h and adequate cooling periods, the chemical problem for the determination of Co, Cr, Ni, P, S, Sc, Ti and Zn traces in iron is related

TABLE XIII

SEPARATION OF ELEMENTS BY ANION EXCHANGE: SHORT-IRRADIATION GROUP (PROCEDURE A)[a]

Element	*% Recovery*			
	9 N HCl+H_2O_2	*2 N HCl+H_2O_2*	*0.5 N HCl+H_2O_2*	*Resin bed*
Mn	99.0±0.5	$\leqslant$0.2	$\leqslant$0.1	0.00
As	100±0	$\leqslant$0.02	0.00	0.00
Cu	$\leqslant$0.1	99.8±0.5	$\leqslant$0.2	0.00
Fe	$\leqslant$0.2	$\leqslant$0.05	99.0±1.1	$\leqslant$0.1
Mo	$\leqslant$4	$\leqslant$0.5	$\leqslant$1	94.2±1.5
W	$\leqslant$2	$\leqslant$0.1	$\leqslant$0.1	98.0±1.8

[a] Experimental conditions: 10 to 100 μg of each element used as carrier; column 200 mm height, 5 mm diameter of Dowex 1X8 resin, 100–200 mesh, conditioned with 9 *N* HCl; elution rate $\leqslant$0.2 ml/min; 10–15 ml collected for all fractions.

TABLE XIV

SEPARATION OF ELEMENTS BY ANION EXCHANGE: SHORT-IRRADIATION GROUP (PROCEDURE B)[a]

Element	*% Recovery*				
	9 N HCl, N_2 atmosphere	*7 N HCl+H_2O_2*	*2 N HCl+H_2O_2*	*0.5 N HCl+H_2O_2*	*Resin bed*
Fe	93.1±2.2	$\leqslant$0.05	$\leqslant$0.02	7.0±0.3	$\leqslant$0.05
Mn	99.2±0.1	$\leqslant$0.2	0.00	$\leqslant$0.1	0.00
As	0.00	100±0.5	$\leqslant$0.1	0.00	0.00
Cu	0.00	$\leqslant$0.02	98.5±1.2	$\leqslant$0.5	0.00
Mo	$\leqslant$2.5	$\leqslant$0.5	$\leqslant$0.2	$\leqslant$0.2	95.5±1.5
W	$\leqslant$0.1	$\leqslant$0.05	$\leqslant$0.1	$\leqslant$0.05	100±1

[a] Experimental conditions: as for Table XIII, but 0.3 to 0.8 g Fe were used as carrier.

to the separation of induced long-lived activities of ^{60}Co, ^{51}Cr, ^{58}Co, ^{32}P, ^{46}Sc and ^{65}Zn from the ^{59}Fe and ^{54}Mn activities arising from the matrix.

The bulk of the iron is previously removed by means of an isopropyl ether extraction (see Table XII), and the anion-exchange procedure schematically described in Table XV is adopted: Mn, Cr, Sc and P are collected in the first washing fraction, while cobalt and zinc are individually separated. The first fraction is submitted to the further procedure illustrated in Table XVI, including an anion-exchange step and solvent extraction for phosphorus, chromium and scandium separations. ^{51}Cr, ^{60}Co and ^{58}Co, ^{46}Sc and ^{65}Zn are counted as solutions, and the different standard geometry is taken into account, as above described. In the case of the β-emitter ^{32}P, G.M. counting and γ-spectrometry (bremsstrahlung radiation) were used for liquid samples, as well as β-spectrometry for solutions evaporated on filter paper disks; the last method is advantageous as a more selective and, when a well-type plastic scintillation is used, a more sensitive technique.

TABLE XV

SEPARATION OF ELEMENTS BY ANION EXCHANGE: LONG-IRRADIATION GROUP[a]

Element	*% Recovery*				
	9 N HCl	*5 N HCl*	*5 N HCl*	*pH 2*	*Bed resin*
Mn	99.0±1.0	≤0.2	≤0.1	≤0.01	0.00
Cr	98.5±2.6	≤0.2	≤0.1	0.00	0.00
Sc	101±2	≤0.1	≤0.05	≤0.04	0.00
P	100±0.5	≤0.01	0.00	0.00	0.00
Co	0.00	99.2±1.2	≤0.15	0.00	0.00
Fe	0.00	≤0.01	99.2±0.5	0.00	0.00
Zn	≤0.05	≤0.03	≤0.05	100±1	≤0.1

[a] Experimental conditions: as for Table XIII.

TABLE XVI

SEPARATION OF P, Cr AND Sc IN THE LONG-IRRADIATION GROUP

Element	*% Recovery*				
	Anion resin pH 5[a]	*1 N HCl elution*[a]	*Molybdophosphoric acid extraction*[b]	*Tribenzylamine extraction*[c]	*Tributylphosphate extraction*[d]
P	98.5±0.9	100±1	99.8±0.8	—	—
Cr	≤0.5	—	≤0.01	96.5±2.1	≤0.5
Sc	≤0.5	—	≤0.05	≤0.3	100±0.5
Mn	≤0.3	—	≤0.05	≤0.2	≤0.9
Fe	≤0.5	—	≤0.1	≤0.5	100±1

[a] Experimental conditions as for Table XIII, but resin conditioned at pH 5.

[b] See ref. 13.

[c] See ref. 14, after oxidation to Cr(VI) with $KMnO_4$.

[d] See ref. 15, after extraction of Fe with isopropyl ether when necessary.

Since for separations of phosphorus, chromium and scandium more than one step is required, including techniques other than simple ion exchange, the chemical recoveries may not be quantitative, especially in routine experiments: the yields are therefore checked, by direct spectrophotometric measurements on aliquots of organic solutions of molybdophosphoric acid, at 310 mμ, and of the chromium(VI)-tribenzylamine complex, at 355 or 458 mμ, while scandium is re-extracted into the aqueous phase and determined as the 8-quinolinol complex (spectrophotometry at 400 mμ). However, no determination of yield is necessary for the cobalt and zinc separations; although the last element is incompletely retained in aqueous solution after the iron extraction step, the constancy of the losses allows the introduction of a correction factor to account for the final recovery without specific evaluations, as confirmed by a preliminary run of tracer experiments.

Cadmium-covered irradiated samples are used as duplicate in sulphur and phosphorus determination, for corrections of spurious contributions in the chromium determinations, for titanium determinations, and in order to reach a higher accuracy in the ^{58}Co counting in the separated fractions of cobalt. In the case of Cd-covered samples, the zinc separation is obviously omitted.

The determination of sulphur and phosphorus is performed by evaluating the contribution of each element to the total ^{32}P activity, through the irradiation of duplicate samples under conditions of different thermal to fast flux ratio (bare and Cd-covered)[16–18]; in Table XVII some results are shown.

The comparison between destructive and direct analysis of the other elements connected with this group is reported in Tables V, IX, and X.

TABLE XVII

DETERMINATION OF P AND S IN IRON SAMPLES

Sample	*Concentration (p.p.m.)*			
	Present[a]		*Found*	
	P	*S*	*P*	*S*
Armco, 99.9	—	—	33.6±1.5	98.0±3.0
BCS 149/1, 99.95	100±10	130±10	99.8±5.2	110±17
Johnson–Matthey, 99.999	—	—	0.30±0.15	1.7±0.5

[a] Certified values.

EXPERIMENTAL

Samples

The iron samples generally consisted of disks, 0.5 mm thick and 5–10 mm in diameter; synthetic samples were prepared by evaporation of aliquots of calibrated solutions on thin pure iron disks. Comparison standards were used both as diluted aluminium alloys and solution evaporated on filter paper disks.

Equipment

The irradiations were carried out in the pneumatic facility of the reactor (thermal flux $4 \cdot 10^{12}$ neutrons/cm^2/sec) for short-lived nuclides, in the thermal column (thermal flux $8 \cdot 10^{8}$ neutrons/cm^2/sec) for a check of the manganese determination and in the pool (thermal flux $4–2.5 \cdot 10^{13}$, fast flux $1.0–0.5 \cdot 10^{13}$ neutrons/cm^2/sec) for the other cases.

Spectrometry measurements were performed with a 200-channel pulse analyzer, Laben C-31, equipped with 3″ × 3″ or 1″ × 0.5 mm NaI (Tl) crystals, or well-type plastic scintillators. Coincidences were counted by means of two 3″ × 3″ scintillation detectors with the source positioned at 2–5 cm distance from each crystal. Counting periods less than 2 min were generally used, but in some cases of low concentration elements coincidences were measured up to 15 min. In order to avoid errors arising from possible surface contaminations, the samples were always etched in nitric acid and washed with water after irradiation.

Procedures

For destructive methods, in the case of the short irradiation group, the samples were dissolved in diluted sulphuric acid, sulphite was used as reducing agent and the anion-exchange procedure reported in Table XIV was carried out after adjusting the solution to about 9 *N* in hydrochloric acid. When long-lived activities were treated, the samples mixed with P, Sc and Cr carriers (100 µg to 10 mg) were dissolved in hydrochloric and nitric acids, the nitric acid eliminated by fuming, and the iron extraction with isopropyl ether was performed after addition of some hydrogen peroxide: the separation procedures as reported in Tables XV and XVI were then carried out, and the chemical yields checked for P, Cr and Sc.

The systematic analytical procedure for iron analysis is schematically illustrated in Fig. 3.

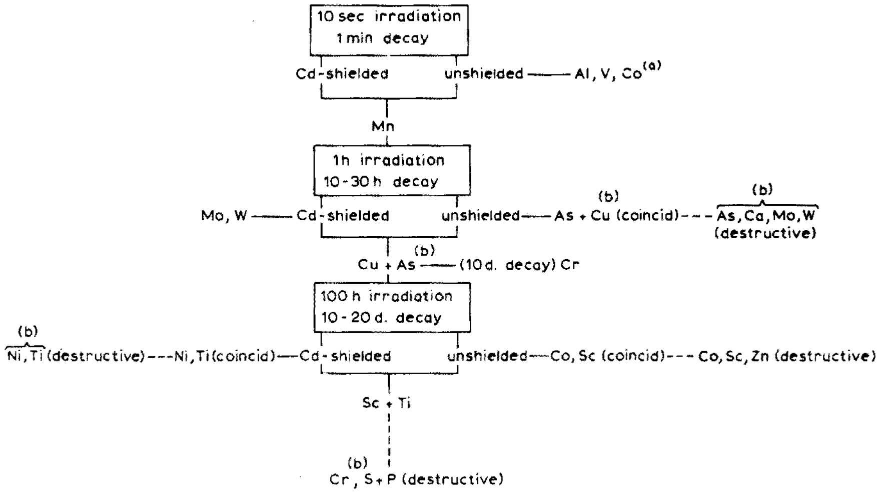

Fig. 3. Analytical procedure for iron analysis. (a) low Mn concentration; (b) element present at lower levels.

DISCUSSION

In both cases of direct and destructive analysis the precision is generally good as shown by replicate determinations; the accuracy was tested by analyzing samples of known composition (standard and synthetic samples): only in the case of manganese determination in 99.999% iron (Johnson–Matthey Specpure standard), a large discrepancy was found, as confirmed by measurements obtained by independent methods.

No important error is connected with the irradiations, as negligible self-shielding effects occur for diluted standard and sample materials, and suitable packing or flux monitoring in the irradiation container are performed in order to account for local flux inhomogeneities. Counting statistics are often the most important factors when low-level activities are measured and relevant background activities are subtracted (Compton, spurious coincidence, etc.); differences between standard and samples must also be considered, especially when β-emitters are measured or in the case of direct counting of low γ-energy activities. Spurious contributions from competing reactions are generally negligible in cases other than the manganese and chromium determinations. An experimental evaluation of this source of error is shown in Table XVIII.

TABLE XVIII

SPURIOUS CONTRIBUTIONS FROM COMPETITIVE REACTIONS

Sought element	*Competitive reaction*	*Interference*[a] *(simulated μg of sought element per g of interfering element)*
Al	$^{31}P\ (n,\alpha)\ ^{28}Al$	$4 \cdot 10^2$
	$^{28}Si\ (n,p)\ ^{28}Al$	$3 \cdot 10^3$
Co	$^{63}Cu\ (n,\alpha)\ ^{60}Co$	4
	$^{60}Ni\ (n,p)\ ^{60}Co$	$\leqslant 6$
Cr	$^{54}Fe\ (n,\alpha)\ ^{51}Cr$	13
Cu	$^{64}Zn\ (n,p)\ ^{64}Cu$	$2.4 \cdot 10^3$
Mn	$^{56}Fe\ (n,p)\ ^{56}Mn$	11.5
	$^{59}Co\ (n,\alpha)\ ^{56}Mn$	2
P	$^{35}Cl\ (n,\alpha)\ ^{32}P$	$2.2 \cdot 10^4$
	$^{32}S\ (n,p)\ ^{32}P$	$1.1 \cdot 10^5$
Sc	$^{46}Ti\ (n,p)\ ^{46}Sc$	17
V	$^{52}Cr\ (n,p)\ ^{52}V$	17

[a] Interferences were evaluated for irradiation in rabbit or in the core center, according to the position used in the analysis.

SUMMARY

A systematic analytical procedure for the determination of some trace impurities in iron matrices was developed by employing both direct and destructive neutron-activation techniques. Irradiations in fast neutron fluxes, selective activation by epithermal neutrons and coincidence γ-spectrometry measurements were used in some cases, in order to improve the sensitivity for non-destructive analysis; for destructive methods, radiochemical separations based on ion exchange and solvent extraction were applied. Procedures are described, and some results of the determination of low concentrations of Al, Mn, Ti, V (non-destructive), P, S, Zn (destructive) and As, Co, Cr, Cu, Mo, Ni, Sc, W (both methods) in iron are reported and discussed.

RÉSUMÉ

Un procédé d'analyse systématique est décrit pour le dosage d'impuretés dans des matrices de fer, utilisant des techniques directes et destructives par activation au moyen de neutrons. Irradiations dans des flux de neutrons rapides, activation sélective par neutrons épithermiques et mesure par spectrométrie-γ ont été utilisées dans certains cas pour améliorer la sensibilité d'analyses non-destructives. Pour les méthodes destructives des séparations radiochimiques, basées sur échange d'ions et extraction par solvant ont été appliquées. Des procédés sont décrits et des résultats sont donnés de dosage de faibles concentrations d'aluminium, de manganèse, de titane, de vanadium (technique non-destructive), de phosphore, de soufre, de zinc (technique destructive) et d'arsenic, cobalt, chrome, cuivre, molybdène, nickel, scandium, tungstène (les deux techniques).

ZUSAMMENFASSUNG

Es wurde ein systematisches analytisches Verfahren zur Bestimmung von einigen Spuren-Verunreinigungen in Eisenmatrizes entwickelt. Dabei wurde sowohl die direkte Neutronenaktivierungstechnik als auch die, bei der anschliessend die Probe zerstört wird, untersucht. Um die Empfindlichkeit der direkten Analyse zu prüfen, wurde im schnellen Neutronenfluss angeregt, selektiv mit epithermischen Neutronen aktiviert und γ-Koinzidenzmessungen angewandt. Bei Zerstörung der Probe, wurden radiochemische Trennungen mit Hilfe von Ionenaustauschern und Flüssigextraktionen verwendet. Die Verfahren werden beschrieben und über einige Ergebnisse der Bestimmung niedriger Konzentrationen von Al, Mn, Ti, V (direkt), P, S, Zn (zerstört) und As, Co, Cr, Cu, Mo, Ni, Sc, W (beide Methoden) in Eisen diskutiert.

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THE ATOMIC ABSORPTION SPECTROSCOPY OF LEAD

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Lead has been determined by atomic absorption in various materials such as gasoline[1], body fluids[2], and wines[3]. For other samples such as foodstuffs, water and air pollution samples, the method has not, up to the present, been sufficiently sensitive for direct determinations. To further its applications a general study of the atomic absorption spectroscopy of lead was undertaken. Important experimental parameters were evaluated and more sensitive analytical procedures are now suggested.

EXPERIMENTAL

Equipment

The atomic absorption instrument used was a Perkin-Elmer Model 303, fitted with a Beckman total-consumption burner. Flow rates of the fuel and oxygen were measured on separate "Hoke" gas flowmeters. A "T"-piece flame adapter was used to provide increased sensitivity; its construction is described elsewhere[4].

Relative sensitivities of lead absorption lines

Three absorption lines can be used for the determination of lead. The relative sensitivity of each line was determined under various conditions and the results are summarized in Table I.

TABLE I

SENSITIVITY LIMITS FOR LEAD USING VARIOUS CONDITIONS AND DIFFERENT WAVELENGTHS

(Flame conditions: Beckman total-consumption burner; H_2 flow rate, 10 l/min; O_2 flow rate, 2.5 l/min)

	Pb concentration for 1% absorption (p.p.m.)		
	2170 Å	*2833 Å*	*4058 Å*
With no adapter			
Aqueous solution	0.45	0.67	150
With "T"-piece adapter[a]			
Aqueous solution	0.047	0.084	
Aqueous solution, reversed flame	0.013		
Aqueous solution plus EDTA (1%)	0.019	0.033	
Aqueous solution plus 50% acetone	0.026	0.040	
Acetyl acetone	0.024	0.035	

[a] Details of the experimental use of the "T"-piece adapter are given later.

As can be seen, the relative sensitivities of the 3 lines are in the ratio 1.0 : 1.5 : 300. For high sensitivity the 2170 Å resonance line should be used and for more concentrated samples the line at 4058 Å is preferable. If the optical range of the equipment used does not extend to the end of the U.V. range (2000 Å), the 2833 Å line should be used. Enhanced sensitivity can be obtained when EDTA is used to complex the lead.

"Reversed" flames

Using a total-consumption burner, it is usual to aspirate the sample with the oxygen used for the flame Unfortunately, this process insures intimate mixing of sample and oxygen and direct oxidation of the sample is facilitated, which in turn usually results in a loss of sensitivity. It was hoped to diminish this effect by switching the flow lines of the oxygen and the hydrogen in the burner so as to use the hydrogen, rather than the oxygen, to aspirate the sample and thus provide a more reducing atmosphere. A reducing atmosphere slows down oxidation of the metal atoms and therefore improves sensitivity.

Results showed that using a "T"-piece adapter and an aqueous solution of EDTA, detection limits were reduced to 0.013 p.p.m. (wavelength 2170 Å).

Effect of solvents

The effect of organic solvents was studied at the optimum 3 wavelengths. The "T"-piece adapter was not used because only relative absorbancies were under consideration.

As observed earlier[1], the use of organic solvents did not particularly enhance the signal. In this respect, lead acts differently from most other metals. Lead is one of the more volatile metals and it is possible that at the temperature of the flame, the lead vaporizes out of the solvent droplets. The rate of production of lead atoms would therefore be a function of the volatility of the lead atoms and would be independent of the solvent type.

Effect of lamp current

It has been reported that the sensitivity for lead is a function of the lamp current used to operate the hollow cathode. Two explanations have been proposed. The first[5] suggests that if a lead alloy is used as the cathode, a higher current must be used to generate a satisfactory lead signal. It is claimed that this improves the signal-to-background ratio and therefore improves the sensitivity of the procedure. The second explanation[6] is that at high currents a cloud of neutral lead atoms is formed inside the hollow cathode. These atoms absorb the center of the line radiated by the hollow cathode. The effect is a change in the spectral characteristics of the emitted resonance line and therefore a change in the quantity of light absorbed by the sample. This type of interference should be common to all volatile metals used in the hollow cathode and the degree of the interference should depend on the design of the hollow cathode and on current used for excitation.

In this study, the hollow cathode used was a standard Ransley hollow cathode. The instrument used was designed to limit the maximum currents available to the various hollow cathodes. In the case of lead hollow cathodes the maximum was about 10 mA.

Studies of the effect of using different current densities were made using aqueous solutions of lead nitrate. The flame used was oxyacetylene at flow rates of (*a*) oxygen, 3.5 l/min and (*b*) acetylene, 2.8 l/min. No special precautions were taken to optimize the conditions, but they were kept constant throughout to make the comparison of data valid. The spectral slit width was kept constant throughout. The results obtained are listed in Table II.

TABLE II

EFFECT OF LAMP CURRENT ON THE SENSITIVITY OF LEAD

Lamp current (mA)	*10 p.p.m. Pb 2170 Å*	*10 p.p.m. Pb 2833 Å*	*4000 p.p.m. Pb 4058 Å*
	Percentage absorption		
3	20.3	14.0	14.9
4	22.0	12.7	8.9
5	20.8	11.5	10.8
6	21.7	11.5	8.5
7	20.7	11.6	11.2
8	21.0	11.6	9.8
9	21.6	11.6	9.8
10	20.4	11.6	11.6

It can be seen from the results that there was no noticeable effect on the sensitivity when the lamp current was changed within the range of the equipment used.

When low lamp currents were used, the voltage to the detector was increased to keep the output energy constant. This increased the noise of the signal significantly, particularly when readings were taken at 4058 Å.

This high noise should be avoided because it causes imprecision in the results. The problem can be solved by using the highest possible lamp currents without causing undue sputtering of the cathode.

Interference studies

The interferences due to other metals have been studied previously. Recent work by DAGNAL AND WEST[7] confirmed that there was no interference from most

TABLE III

EFFECT OF SELECTED CATIONS ON LEAD ABSORPTION

(Conditions: Flame: H_2, 30 l/min and O_2, 4.7 l/min; wavelength: 2170 Å)

Interfering element (500 p.p.m. each)	*Total absorption (%)*				
	Flame alone	*Flame and water*	*Flame and interfering element (500 p.p.m.)*	*Flame plus Pb (10 p.p.m.)*	*Flame plus interfering element (500 p.p.m) plus Pb (10 p.p.m.)*
Al	6.2	6.2	6.2	28.0	28.0
Be	6.4	6.4	6.4	28.0	28.0
Zr	7.4	7.4	7.4	28.0	28.0
Th	7.2	7.2	7.2	28.1	28.1
Na	7.2	7.2	7.2	28.4	28.4
K	7.2	7.2	7.2	28.5	28.5

cations. However, they did report interferences from aluminum, beryllium, zirconium and thorium which warranted further investigation. The effects of these metals were therefore examined using a Beckman burner with no flame adapter. Results are shown in Table III.

Interference studies were also carried out at wavelengths of 2833 Å and 4058 Å. No interference was found at any of the wavelengths studied from solutions containing 500 p.p.m. of Al, Be, Zr or Th. It is possible that the difference in results can be attributed to the fact that the equipment used for the studies reported herein was modulated and therefore free from radiation interferences. However, it must be pointed out that DAGNAL AND WEST used a cooler flame in their studies. Chemical interference is more prevalent in cooler flames and this may explain the interferences they noted.

Interference from high salt concentration

Interference was noted from many cations at concentrations in excess of 2000 p.p.m. It was felt that such interference was different in nature from chemical interference which is usually caused by a difference in bond strength between the metal (lead) and the anion. In this instance the interference was not caused by anions, but by the cations present. For chemical interference from cations to take place, intermetallic compounds must be formed in the flame. Any intermetallic compound formation would be noted even at low metal concentration levels. An alternative explanation of this interference at high concentrations may be as follows.

In the process of forming neutral atoms in the flame, the following sequence of events may occur. The sample is aspirated into the flame as water droplets. These droplets evaporate leaving a salt residue which is then decomposed, liberating neutral metal atoms. If the interfering salt concentration in the residue is high, the concentration of lead must be relatively low. Much of the energy received by the residue will therefore be used in decomposing the salt, and the quantity of lead liberated will be lessened.

For example, a given flame may generate enough energy to evaporate aspirated sample droplets and to decompose 100 μg of the residue, per unit time. If this residue is composed of lead salts, the efficiency of producing lead atoms would be high. However, if most of this residue is the salt of another metal, the lead salts will be only a minor component of the residue. The efficiency of producing lead atoms in the flame would be reduced and a non-selective interference would result.

This non-selective type of interference can be expected whenever high salt concentrations are present. It can be a problem whenever salt baths, or strong solutions of pure salt are analyzed directly. It can be eliminated by dilution, if the lead content is high enough. Otherwise, extraction and concentration of the lead may be necessary.

Anionic interference

The interference of various anions on lead was examined. Results are shown in Table IV. These indicate that each different anion produced a change in the absorption signal of the lead. This interference has been attributed to chemical interference. The addition of EDTA to the solution eliminated this interference with the anions tested.

TABLE IV

ANIONIC INTERFERENCES

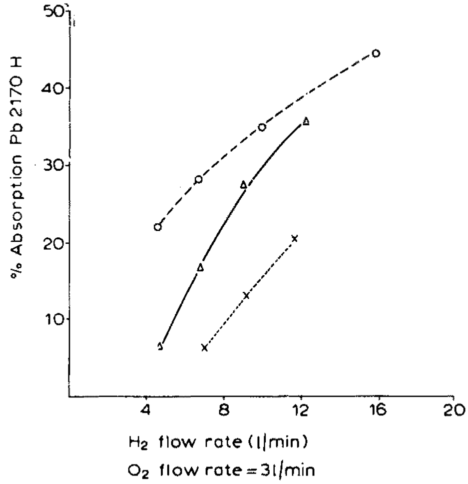
(Conditions: Flame: O_2, 10 l/min and H_2, 2 l/min; wavelength: 2170 Å)

Interfering anion (100 p.p.m.)	*Percentage absorption*	
	Lead nitrate (10 p.p.m.) plus interfering anion	*Lead nitrate (10 p.p.m.) plus interfering anion plus EDTA*
NO_3^-	23.0	23.0
PO_4^{3-}	19.9	22.8
Cl^-	22.3	22.3
CO_3^{2-}	12.8	23.0
I^-	13.7	23.5
SO_4^{2-}	22.0	23.0
F^-	21.3	22.9

Studies on the use of flame adapters

The use of "T"-piece flame adapters has been reported earlier[1], but they have not been investigated extensively. Subsequent workers[8] have been able to obtain considerable absorption enhancement by using long flame adapters. Studies have been made of some of the variables that affect the absorption by the products of combustion of the flame and the solvents. For reproducible results careful control of conditions must be exercised.

The "T"-piece used was similar to that described earlier[1]. The hot products of the flame were prevented from entering the optics of the instrument by using an air jet. This proved to be troublesome and unreliable. Washable quartz windows fitted to the optic ports of the instrument in addition to the air jets were found to be preferable.



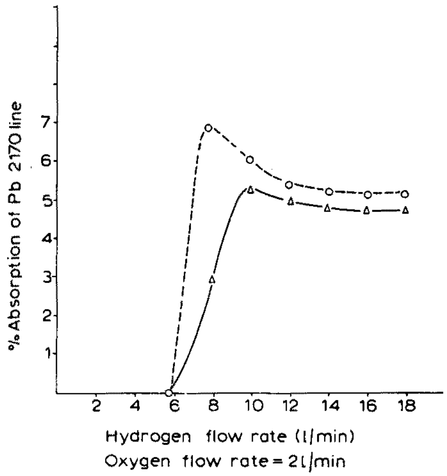


Fig. 1. Absorption by flame, alone, and with aqueous and organic solvents. --○--, absorption of flame burning organic solvent; —△—, absorption of flame alone; ...×..., absorption of flame plus aqueous sample.

Fig. 2. Effect of EDTA on the absorption of lead. --○--, 0.1 p.p.m. Pb in 1% EDTA aqueous solution; —△—, 0.1 p.p.m. Pb in aqueous solution.

Results. It was found that the sensitivity in aqueous and organic solvents was about 0.013 p.p.m. (for 1% absorption). No interference from cations on the lead absorption was noted. Anionic interferences were eliminated using EDTA. The sensitivity limits conceivably could be reduced to 1 p.p.b. by prior solvent extraction of the lead. Considerable interference was found from the products of combustion of the flame and solvents aspirated into the flame. This absorption was changed drastically by variation in the oxygen to fuel ratio. A study was made at 2170 Å of a 0.1 p.p.m. aqueous solution of lead nitrate. A Beckman total consumption burner was employed and the ratio of the oxygen and hydrogen flow rates was varied extensively. The absorption of (*a*) the flame, (*b*) the aqueous solvent and (*c*) the products of combustion of organic solvents were recorded. Results are shown in Fig. 1.

It can be seen that absorption of the 2170 Å line was significantly influenced by all 3 variables. Further, there was wide variation in the extent of absorption as the oxygen–hydrogen ratio was varied.

Using the same system, the absorption of lead was studied in the presence and absence of EDTA. Figure 2 summarizes the results.

Absorption of lead in aqueous solution

The absorption by lead was sensitive to flame conditions, but there was a workable range of oxy–hydrogen ratios where the lead absorption was relatively insensitive to such changes. The absorption by the combustion products of EDTA was significant and was susceptible to changes in flame composition.

Absorption of oxy–acetylene flames

Similar studies were made with oxy–acetylene flames. Two "T"-pieces were

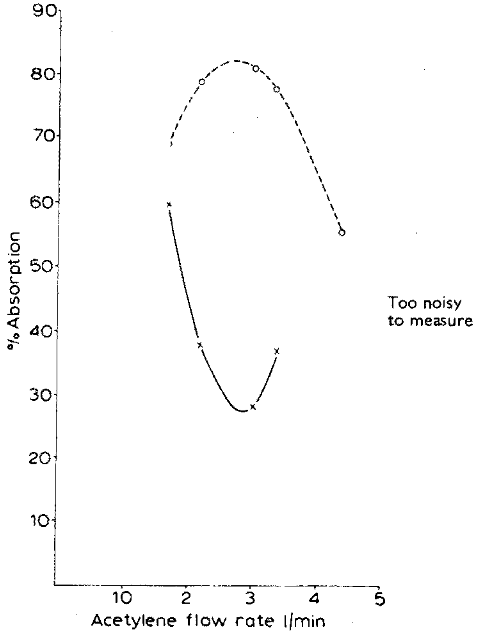


Fig. 3. Absorption of oxy–acetylene flame products in "T"-piece adapter. --○--, oxygen 4 l/min; —×—, oxygen 3 l/min.

used, each with a side-arm of different length. Results showed that the length of the side-arm affected the extent of absorption by the flame. Absorption data were measured at numerous pressures of oxygen and acetylene. Typical results are summarized in Fig. 3.

The absorption by the flame was extensive, reaching 81% in one instance. It also varied extensively with flame composition. Further, the extent of absorption was not only dependent on the ratio of oxygen to acetylene, but also on the actual flow rates involved. For example, the flame absorption was markedly different at oxygen–acetylene flow rates of 2:2 l/min and 3:3 l/min, even though the ratios were the same in each case.

The absorption by solvent combustion products was very high, particularly when organic solvents were used.

In reducing flames, the "T"-piece became brilliantly white. The instrument read-out became very noisy and erratic. The results obtained under these conditions were unreliable, but did indicate that this was not a useful analytical range when flame adapters are used. Probably the light radiated from the "T"-piece overloaded the detector and caused an erratic response.

RECOMMENDED PROCEDURES

Sample preparation. All samples must be converted to the liquid form before the determination. Solid samples should be decomposed if necessary and dissolved, preferably in nitric acid.

Aqueous solution. The lead in clear aqueous solution may be determined directly over a considerable concentration range. Suitable calibration curves have been obtained over the following ranges

Absorption wavelength (Å)	*Range (p.p.m.)*
2170	0.1– 1.0
2833	0.5–10.0
4058	No data (300 p.p.m.+)

Slit width: 2.0 Å.

Flame: oxy–hydrogen or oxy–acetylene.

Interferences. These are numerous, but can be removed by adding EDTA to the sample (1 g/100 ml). A correction for the effect of high concentration of salts must be made in the calibration curve.

TABLE V

PRECISION DATA

Absorption wavelength (Å)	*Pb concn. (p.p.m.)*	*Flame*	*No. of detns.*	*2σ (p.p.m.) 95% confidence*
2170	0.1	O_2–H_2	14	0.03
2170	1.0	O_2–H_2	15	0.07
2833	1.0	O_2–C_2H_2	11	0.08
2833	10.0	O_2–C_2H_2	17	0.6
2833	20.0	O_2–C_2H_2	16	0.5

Precision data. The data shown in Table V were obtained using a Perkin Elmer 303 atomic absorption spectrophotometer.

For samples in which the lead concentration is lower than 0.1 p.p.m., the following extraction procedure may be used.

Lead in air

Sampling and dissolution. Trap lead on an iodine column and/or a millipore filter, depending on the state in which the lead is present in the air[9]. Extract the trapped lead with a suitable solvent (*e.g.*, an acid or aqueous potassium iodide solution) so that 1–10 μg (or higher amounts) of lead is obtained in a volume of *ca.* 20 ml of the solution. Proceed as outlined under *Determination.*

Lead in water

Sample. Take 25–250 ml of water containing from 1–10 μg (or higher amounts) of lead. Proceed as outlined under *Determination.*

Determination. Add 4 ml of a saturated aqueous solution of potassium iodide and enough concentrated hydrochloric acid (s.g. 1.19) to make 5% (v/v) of the total volume. Extract with 10 ml of methyl isopropyl ketone. Run a reagent blank through the entire procedure. Measure the absorption at 2170 Å, using a lamp current of 8 mA, and a spectral slit width of 2 Å. Aspirate the organic extract into an oxy–hydrogen flame produced by a single integral aspirator burner (Beckman) fitted on the top with a long-path (7-in.) adapter[7], using a hydrogen flow rate of 5 l/min and an oxygen flow rate of 2.8 l/min. Set the atomic absorption spectrophotometer to read 0% absorption with pure methyl isopropyl ketone sprayed into the flame. Read the absorption of the reagent blank and subtract its optical density from that of the samples (or the standards). Prepare a calibration curve with 1–10 μg of lead extracted into 10 ml of methyl isopropyl ketone, following the above procedure. Read the concentration of the unknown sample from the calibration curve.

For accurate work, a check on the calibration curve should be made daily in order to compensate for the effect of any variation in atomizer and burner efficiency.

Since lead is distributed uniformly in the 10 ml of methyl isopropyl ketone used for extraction, a slight emulsification and consequent slight loss in the recovery of the MIPK in the process of solvent extraction does not appreciably affect the results, if care is taken not to draw off any emulsion or water with the organic phase. During extraction, vigorous shaking is neither necessary nor desirable as it produces an emulsion which delays phase separation.

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SUMMARY

Lead can be determined by atomic absorption spectroscopy at 3 wavelengths. The relative sensitivities are 1:1.5:300. No interferences were found from the cations studied. Anionic interferences were numerous and extensive, but were removed by adding EDTA. The use of a "T"-piece increased the sensitivity of atomic absorption

when flame atomizers were used. However, extreme care was necessary in controlling flame conditions both with respect to oxygen–fuel ratio and the type of solvent used. The absorption by combustion products in the flame was high, and in many cases, much greater than that of the lead itself.

The most sensitive conditions for the determination of lead appeared to be as follows: wavelength, 2170 Å; solvent, aqueous or organic; flame, oxy–hydrogen, with the hydrogen atomizing the sample (reversed from normal). A flame adapter enabled detection limits of 0.013 p.p.m. to be reached.

RÉSUMÉ

Le plomb peut être dosé par spectroscopie par absorption atomique, à 3 longueurs d'onde (sensibilités relatives: 1:1.5:300). Aucune interférence n'a été observée avec les cations examinés. Les interférences anioniques sont nombreuses, mais facilement éliminées par l'EDTA. L'emploi d'un "T" augmente la sensibilité d'absorption atomique. Cependant, l'absorption par les produits de combustion de la flamme est forte et dans de nombreux cas supérieure à celle du plomb lui-même. Les conditions optima sont les suivantes: longueur d'onde 2170 Å, solvant aqueux ou organique, flamme oxy–hydrogène avec l'hydrogène atomisant l'échantillon.

ZUSAMMENFASSUNG

Blei kann mit der Flammenabsorptions-Spektroskopie bei 3 Wellenlängen bestimmt werden. Die relativen Empfindlichkeiten betragen 1:1.5:300. Für die untersuchten Kationen wurden keine Störungen gefunden. Störungen durch Anionen waren zahlreich, konnten aber durch Zugabe von EDTA beseitigt werden. Die Anwendung eines "T"-Stückes steigert die Empfindlichkeit der Atomabsorption, wenn Flammenzerstäuber benutzt werden, jedoch ist besondere Sorgfalt bei der Kontrolle der Flammenbedingungen nötig, sowohl in Hinsicht auf das Sauerstoff–Brennstoffverhältnis als auch bei der Wahl des Lösungsmittels. Die Absorption der Verbrennungsprodukte in der Flamme war hoch und in vielen Fällen grösser als die des Bleis. Die optimalen Bedingungen zur Bestimmung von Blei scheinen folgende zu sein: 2170 Å, wässriges oder organisches Lösungsmittel, Sauerstoff–Wasserstoff-flamme mit einer Wasserstoffzerstäubung in der Probe. Mit einem Flammenadaptor können Nachweisgrenzen von 0.013 p.p.m. erreicht werden.

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BEITRÄGE ZUR MIKROCHEMISCHEN ANALYSE LANGLEBIGER URANSPALTPRODUKTE IN STAUBPROBEN

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Eine Gesamtaktivitätsmessung von Luft, Wasser und Nahrungsmitteln als alleinige Überwachungsmethode der Strahlenbelastung des Menschen ist nur dann berechtigt, wenn sich die Gesamtaktivität unter der maximal zulässigen Konzentration des gefährlichsten Nuklids befindet. Die Gefährlichkeit der Radionuklide auf den Organismus ist einerseits von Strahlungsart, Strahlungsenergie und Halbwertszeit, anderseits von der möglichen Anreicherung in bestimmten Organen des Menschen abhängig. Bei der Gefahr einer Inkorporation ist vor allem die Kenntnis der Natur des Strahlers bzw. die Zusammensetzung des Nuklidgemisches notwendig, um die Möglichkeit der Anreicherung des Nuklids in bestimmten Organen zu wissen und entsprechende Gegenmassnahmen zu treffen. Aus der Kenntnis des Nuklids ergibt sich auch die Gefährlichkeit für den Menschen, wobei als "Maximal zulässige Konzentrationen"[1] der einzelnen Radio-Isotope Werte bestimmt und festgesetzt wurden, die bei Dauerbelastung den Menschen nach dem heutigen Stand der Kenntnis noch nicht gefährden.

TABELLE I

Nuklid	$t_{\frac{1}{2}}$	*Zerfällt in*	$t_{\frac{1}{2}}$	*Stabil*
^{144}Ce	285 d	^{144}Pr	17.3 m	^{144}Nd
^{137}Cs	30 a	^{137m}Ba	2.6 m	^{137}Ba
^{106}Ru	1 a	^{106}Rh	30 s	^{106}Pd
^{90}Sr	28 a	^{90}Y	64.5 h	^{90}Zr
^{95}Zr	65 d	^{95}Nb	35 d	^{95}Mo

Radioaktiv verunreinigte Luft gefährdet den Menschen sofort und unmittelbar. Eine Analyse soll daher mit möglichst wenig Aufwand und Probenmaterial Aufschluss über die Zusammensetzung der Gesamtaktivität geben. Die Aktivität, die bei Kernbombenexplosionen in die Luft gelangt, kondensiert rasch an vorhandenes Aerosol. Rund 80% der Energie wird dabei in Bewegungsenergie der Teilchen umgesetzt, wobei Aktivitäten bis in die Stratosphäre geschleudert werden; dort kreisen sie um die Erde und fallen erst im Laufe von einigen Jahren wieder auf die Erdoberfläche aus. Die Grösse des radioaktiven Aerosols von 1 bis 5 mμ liegt in der Grössenordnung des Resorptionsintervalls der Lunge, so dass es zu einer Speicherung und Sammlung der Radionuklide und somit zu einer hohen punktförmigen Strahlenbelastung des betroffenen Gewebes kommt. Auf dem Wege über den Boden, Wasser und Pflanze gelangen Radionuklide in unsere Nahrungsmittel und tragen damit erheblich zur Strahlenbelastung bei.

In Tabelle I sind die im atmosphärischen Niederschlag am häufigsten vorkommenden langlebigen Radionuklide zusammengefasst.

Es war das Ziel der vorliegenden Arbeit, für diese Nuklide eine möglichst einfache analytische Arbeitsmethode zu schaffen, die sich auch als Feldmethode einsetzen lässt und die die Trennung und die quantitative Bestimmung der radioaktiven Nuklide des Luftaerosols durchzuführen gestattet, wobei von vornherein auf aufwendige und teure Gerätschaften verzichtet wurde.

Die Schwierigkeit einer Bestimmung der die Strahlung verursachenden Nuklide liegt auf der Hand. Eine chemische Bestimmung benötigt, wegen der ausserordentlich geringen Menge an strahlendem Nuklid neben einem grossen Überschuss an Ballaststoff, grosse Probenmengen und eine besondere spurenanalytische Arbeitstechnik. Die MZK für $^{90}Sr + ^{90}Y$ beträgt z.B. $1 \cdot 10^{-9}$ mg/m^3 oder $2 \cdot 10^{-10}$ C/m^3 Luft. Auch eine physikalische Bestimmung, wie die Gammaspektroskopie benötigt grössere Aktivitätsmengen zur Bestimmung. Die Grenzen der Gammaspektroskopie bei überdeckten Peaks sind bekannt; β-Strahler wie das gefährliche Strontium-90 werden nicht registriert. Der Einsatz dieser Geräte an Katastrophenstellen, abgesehen von den hohen Anschaffungskosten, ist nicht leicht durchzuführen. Methoden zur Isolierung und Bestimmung einzelner Radionuklide sind in der Literatur in grosser Zahl beschrieben. Weiters sind auch einige Methoden zur systematischen Auftrennung von Spaltproduktgemischen angegeben, die sich den Methoden der Spurenanalyse bedienen, seien es Ionenaustauschermethoden[2,3], Extraktion[4] oder Papierelektrophorese[5]. Die Methoden benötigen entweder grosse Probenmengen oder werden durch grössere Ballaststoffe, wie sie in natürlichen Proben vorkommen, gestört.

Die Ringofentechnik[6], die als Analysenmethode mit z.B. autoradiografischer Endbestimmung für radioaktives Material sehr gut geeignet ist[7,8] wurde auch zur Analyse von Radionuklidgemischen herangezogen[9,10].

WEISZ UND KLOCKOW[10] geben einen qualitativen Trennungsgang für Uranspaltprodukte mittels der Ringofenmethode an. Durch eine Folge geeigneter Fällungs-, Umfällungs-, Demaskierungs- und Auswaschschritte werden nacheinander einzelne Nuklide bzw. Nuklidgruppen aus dem zentralen Tüpfelfleck eines Rundfilters in verschiedene Ringe konzentriert. Die Methode wurde an einer synthetischen Probelösung reiner Nuklide, mit Zusatz von 0.1 mg/ml Träger, aber ohne begleitende Ballaststoffe, wie sie in natürlichen Proben vorkommen auch quantitativ ausgewertet. Es zeigte sich, dass eine 50 prozentige ($^{90}Sr/^{90}Y$) bis 99.4 prozentige ($^{137}Cs/^{137m}Ba$) Abtrennung möglich ist.

Im Folgenden wird ein einfach durchzuführender Trennungsgang für langlebige Uranspaltprodukte in Staubproben beschrieben, wobei der Aufschluss, die Trennung und die qualitative und quantitative Bestimmung mit geringsten Mengen natürlicher Staubproben praktisch mit Erfolg erprobt wurden.

Staubsammlung

Während der Zeit der Kernexplosionsversuchsserien der Grossmächte, wurden von November 1961 bis Juni 1962 mit einer Wasserstrahlpumpe täglich rund 4.5 m^3 Luft durch ein Weissbandfilter SS 589^2 von 22 mm Durchmesser angesaugt. Das Filter wurde täglich gewechselt und seine Sofortaktivität und Fünftageaktivität bestimmt. Das verwendete Filter erwies sich bei der geringen Strömungsgeschwindigkeit und Staubbeladung als ausreichend für eine quantitative Abscheidung des Luftaerosols. Die mittlere Staubbeladung des Filters betrug 0.22 mg/m^3 Luft bei einer gassenseitigen Ansaugung vom dritten Stock des Institutes für Analytische Chemie und Mikrochemie der Technischen Hochschule Wien.

Eine Vergleichsuntersuchung[11] über 12 Monate hinaus hat gezeigt, dass diese Art der Probennahme mit der über grosse Geräte erfolgten durchaus vergleichbar ist.

Zur Analyse der radioaktiven Aerosole ist es vorerst wichtig diese in Lösung zu bringen, um dann durch eine geeignete Analysenmethode eine Trennung in die vorhandenen Nuklide durchzuführen.

Aufschluss des Staubes

Wie Versuche zeigten[11] lässt sich der Staub quantitativ und schnell durch einen Schmelzaufschluss aufschliessen. Es wurde in Fortführung der Arbeit von Koch, Malissa und Ditges[12] eine Methode entwickelt, die es gestattet in einem Arbeitsgang das Staubsammelfilter zu veraschen und den Staub in einer Schmelzperle aufzuschliessen.

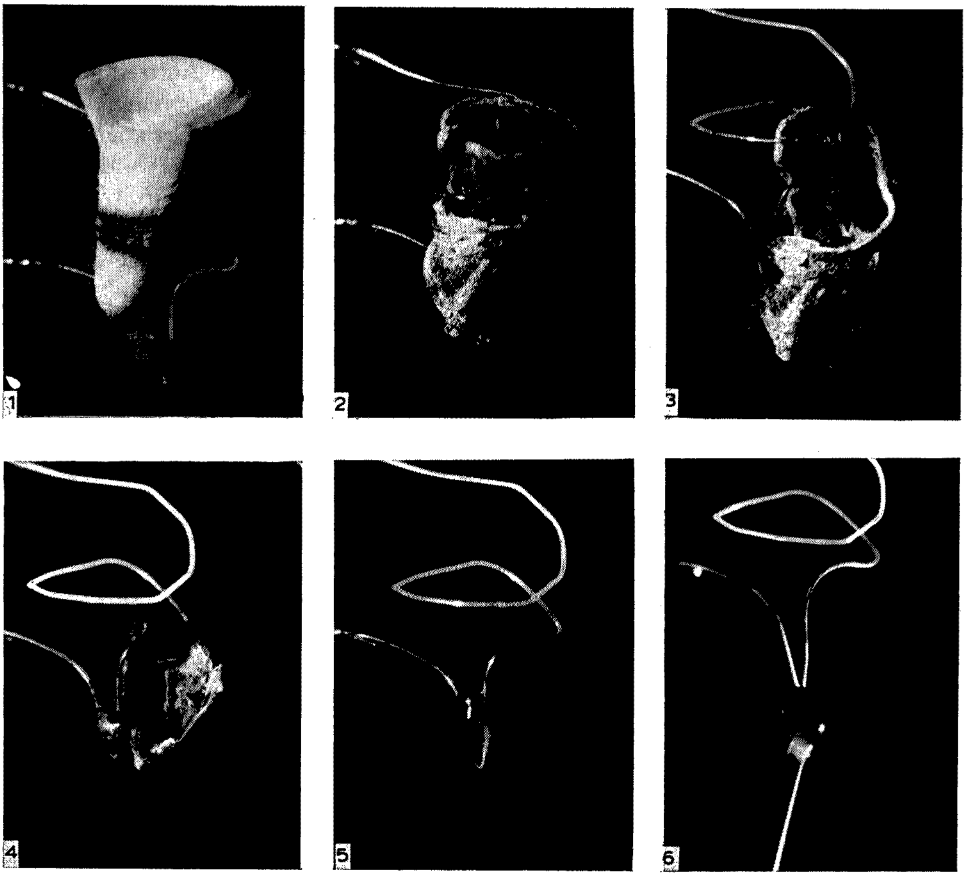

Fig. 1. Veraschung eines Staubsammelfilters und Aufschluss des Staubes in der Schmelzperle.

Das Staubsammelfilter wird mit seiner staubbeladenen Fläche nach innen zweimal über Kreuz gefaltet und dann eingerollt in eine elektrisch regelbar heizbare Platinspirale geschoben wie es Fig. 1 zeigt. Das Filter wird mit 10 bis 20 μl Trägerlösung und mit einer wässrigen Lösung des Aufschlussgemisches befeuchtet. Als Trägerlösung wurde eine wässrige Lösung mit 0.1 mg/ml inaktiver Träger für die Nuklide Cs, Sr, Y, Ce, Ru, Zr und Nb als Nitrate oder Chloride verwendet. Eine Nioblösung bereitet man, da Oxalate und Fluoride wegen der Fällung von Strontium und Cer vermieden werden müssen, nach einer Methode wie sie TREADWELL[13] angibt: Niobpentoxid wird mit Kaliumkarbonat aufgeschlossen. Die Schmelze wird mit Wasser ausgelaugt und mit Salzsäure angesäuert, wodurch Niobsäure milchig ausfällt, die sich beim Neutralisieren mit Ammoniak zu fahlgelben Flocken zusammenballt. Es wird filtriert und mit halbprozentigem Ammoniak gewaschen. Die Niobsäure ist in Salzsäure unlöslich, beim Kochen mit konzentrierter Salzsäure geht wenig in Lösung, aber der Rückstand nach dieser Behandlung ist leicht wasserlöslich. Die auf diese Weise hergestellte Nioblösung bleibt auch auf lange Zeit klar.

Als günstigstes Aufschlussmittel für den Staub und zur Bildung einer klaren Schmelzperle hat sich ein Gemisch von Borax und Natriumkarbonat 1:1 gezeigt[11]. Durch das Anfeuchten des Filters mit der Lösung des Aufschlussgemisches wird beim langsamen Erhitzen der Platinspirale mit dem noch feuchten Filter jeglicher Verlust durch abfallende Asche vermieden, da diese durch die sich bildende Schmelzhaut am Draht hängen bleibt. Durch Temperatursteigerung sammeln sich die feinen Schmelzentröpfchen in der dafür ausgebildeten Spitze der Platinspirale. Es wird dann noch ungefähr zwei Minuten bis zur völligen Klarschmelze erhitzt und die schmelzende Perle durch Berühren mit einem Glasstab vom glühenden Platindraht abgezogen. Die Phasen der Veraschung und des Aufschlusses werden in Fig. 1 gezeigt.

Anreicherung am Ringofen

Die Perle wird in ein Spitzröhrchen übertragen und durch leichtes Pressen gegen die innere Wand des Spitzröhrchens springt sie vom Glasstab ab. Sie wird in 4 Tropfen 4 *N* Salzsäure bei gelindem Erwärmen gelöst. Nach Verdünnen mit 6 Tropfen Wasser wird die Lösung auf einem Chromatografiepapier SS 2043 b im Ring angereichert. Das Spitzröhrchen wird mit 3 Tropfen 0.1 *N* Salzsäure nachgespült und diese ebenfalls in den Ring gebracht. Die während der Anreicherung zur Seite geschwenkte Waschpipettenhalterung des Ringofens wird jetzt zur Mitte geschwenkt und mittels der Waschpipette mit 0.1 *N* Salzsäure drei bis viermal nachgewaschen. Das unter der Heizlampe getrocknete Filter enthält jetzt im Ring alle im Staub vorhandenen Nuklide in löslicher Verbindung.

Bei der Anreicherung von Lösungen mit einer grösseren gelösten Salzmenge, wie es hier durch Lösen einer Perle in einigen Tropfen Flüssigkeit der Fall ist, ist es notwendig ein Papier am Ringofen zu verwenden, das diese Salzmenge im Ring aufnehmen kann. Ausserdem soll dieses Papier gut saugen und soll im Hinblick auf eine quantitative Auswertung nach der hier angewendeten Methode keine bevorzugte Saugrichtung aufweisen und somit eine gleichmässige Konzentrationsverteilung über den Ring bewirken. Fabrikationsbedingt weist jedes maschinell erzeugte Papier eine sogenannte Laufrichtung auf. Infolge der erheblichen Wasserströmung auf der Papiermaschine richten sich im Verlauf der Blattbildung die Fasern bevorzugt in der Richtung des Wasserflusses aus, die Saugung in dieser Richtung ist daher immer etwas grösser als in der dazu senkrecht stehenden. Da im Handel kein handgeschöpftes Papier erhältlich war, wurden verschiedene maschinell erzeugte Papiere auf ihre Gleichmässigkeit in der Substanzverteilung untersucht. Den gewünschten Anforderungen entsprach das Schleicher und Schüll Chromatografiepapier 2043 b noch am besten. Die Salzaufnahme ist durch das hohe Flächengewicht von 120 bis 125 g/m^2 sehr günstig. Perlen bis 4 mg (1.5 mm Durchmesser) lassen sich auf diesem Papier noch einwandfrei in einen haltbaren Ring bringen.

Versuche mit dem Borax-Sodagemisch und mit Staubasche ergaben, dass bis zu einem Gewichtsverhältnis von Aufschlussgemisch zu Staubasche wie 1 zu 1 der Aufschluss noch einwandfrei gelingt. In diesem Fall schmilzt die Perle allerdings schon sehr zäh und es ist zum Lösen eine 6 *N* Salzsäure erforderlich. Es ist daher ratsam in einer Perle von 4 mg möglichst 2 mg Staubasche nicht zu überschreiten.

Zur Anreicherung der Lösung am Ringofen kann die schon beschriebene Apparatur[9] verwendet werden. Wegen der hohen Saugkraft des Chromatografiepapiers genügt jedoch eine vereinfachte Vorrichtung, wie sie die Fig. 2 zeigt.

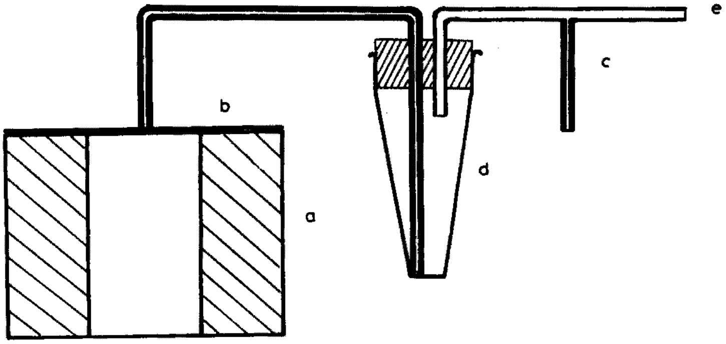

Fig. 2. Methode zur Anreicherung der Lösung am Ringofen. (a) Ringofen; (b) Filter; (c) Kapillarrohr; (d) Spitzröhrchen; (e) Anschluss der Gummiballpumpe.

In dem doppelt durchbohrten Gummistoppel des Sitzröhrchenverschlusses sitzt einerseits ein Heber aus Kapillarrohr, wobei allerdings das Flüssigkeitsniveau im Spitzröhrchen tiefer liegt als das Auslauf-Ende der Kapillare am Filter des Ringofens, anderseits ein Glasrohr, das sich in zwei Enden gabelt, an dessem einen Ende eine Gummiballpumpe hängt, während das andere Rohrende verjüngt ist, und offen bleibt. Das Spitzröhrchen wird in einer lockeren Führung an einem Stativ gehalten, wobei das äussere Kapillarende am Ringofen in der Mitte des Filters senkrecht aufsitzt und durch die eigene Schwere des Ganzen an dieses angedrückt wird. Durch Pumpen mittels der Gummiballpumpe wird nun stossweise ein gelinder Überdruck in dem System erzeugt, wobei die Luft durch das offene Rohrende entweicht, die Flüssigkeitssäule in der Kapillare aber dabei gegen das Filter gedrückt wird. Die kapillare Saugkraft des Filters ist nun so gross, dass Niveauunterschiede von 1 bis 2 cm überwunden werden und die Flüssigkeit aus dem Spitzröhrchen abgesaugt wird, so wie sie im Ring verdampft. Eine Flüssigkeitsmenge von einem halben Milliliter wird in *ca.* 4 Minuten im Ring verdampft.

TRENNUNG DER NUKLIDE

Als Prinzip der Trennung wurde die spezifische Fällung jedes einzelnen Nuklides in einem Ringsektor gewählt, nach dessen Fixierung alle anderen in diesem Sektor unerwünschten Nuklide ausgewaschen werden. Versuche zeigten, dass ein Fällungsbad zur Fällung eines Nuklids zwar genügt, aber nicht ausreicht, die anderen Nuklide quantitativ auszuwaschen. Es wurde daher nach dem entsprechenden Fällungsbad ein Waschbad nachgeschaltet. Bei der geringen effektiven Menge an Nukliden, die trotz Trägerzusatz im Ring vorhanden sind, wurden nach dem Baden im Fällungsreagens, je nach der Löslichkeit der gefällten Verbindung mehr oder weniger grosse Verluste festgestellt. Diesen wurde durch Versetzen aller Bäder mit Bodenkörper der entsprechenden inaktiven Fällungsform begegnet, wodurch eine Sättigung der Bäder erreicht wurde und beim Baden des Filters das radioaktive Nuklid in gefällter Form quantitativ im Filter verblieb.

Um in einem Ring alle Nuklide bestimmen zu können, wird dieser mittels einer Schablone in 6 gleiche Sektoren zerschnitten. Ein Sektor bleibt jeweils unbehandelt und dient als Vergleichssektor. Die anderen Sektoren werden jeder für sich in den für das zu bestimmende Nuklid vorbereiteten Bädern je einige Minuten gebadet. Danach werden sie unter der Heizlampe getrocknet und nach Aufkleben auf Karton und Abdecken mit einer Plastikfolie (bei der nachfolgenden Trennung wurde eine Folie von 2.8 mg/cm^2 Flächengewicht verwendet) autoradiografiert. Bei Arbeiten mit höheren Aktivitäten kann natürlich eine instrumentelle Auswertung erfolgen.

Autoradiografie

Eine autoradiografische Aktivitätsbestimmung bietet die Möglichkeit noch Aktivitäten quantitativ auszuwerten, die einer instrumentellen Auswertung wegen des ungünstigen Signalrauschverhältnisses nicht mehr zugänglich sind[8,9].

Film: Kodak Kodirex X-Ray Film.

Entwickler: Kodak DX-80.

Entwickelt wurde bei 20°, 4.5 Minuten im unbeleuchteten Raum bei zeitweiliger Bewegung des Films.

Sehr günstig bei dieser Arbeit erweisen sich die rostfreien Zahnfilmentwicklerklammern, an denen der Film während der Entwicklung, Zwischenwässerung, Fixierung, Hauptwässerung und Trocknung hängen bleiben kann. Während der Exposition ist es notwendig die Filter, die noch Chemikalienreste anhaften haben, mit einer möglichst dünnen Plastikfolie zu bedecken, damit durch den engen Kontakt keine Schädigung der Schicht eintritt.

Für die einzelnen Nuklide kamen folgende Bäder zur Anwendung.

Cäsium-137

Fällungsbad. 5% Platinchlorwasserstoffsäure in 0.5 *N* Salzsäure mit einem Bodenkörper von inaktivem Cäsiumhexachloroplatinat.

Waschbad. 2 *N* Salzsäure mit inaktivem Cäsiumhexachloroplatinat als Bodenkörper.

Bemerkung. Die aktive Tochter Barium-137m wird nicht mitgefällt, das Gleichgewicht ist aber nach 10 Halbwertszeiten wieder eingestellt, das heisst, dass nach 26 Minuten die abgetrennte Tochter zerfallen ist und das Cäsium eine neue Tochtersubstanz nachgebildet hat.

Strontium-90

Fällungsbad. 100 ml 50% Äthanol und 25 ml 2 *N* Schwefelsäure. Als Bodenkörper wird noch inaktives Strontiumsulfat zugesetzt oder durch Zugabe von wenigen Tropfen Strontiumnitratlösung gebildet.

Waschbad. 0.5 *N* Schwefelsäure mit etwas Strontiumsulfat als Bodenkörper.

Bemerkung. Bei der Fällung des Strontium-90 als Sulfat wird die Tochtersubstanz, das Yttrium nicht gefällt. Yttrium-90 mit seiner Halbwertszeit von 64.8 Stunden ist nach 7 Halbwertszeiten oder 19 Tagen zu 99% nachgebildet, während die abgetrennte Tochter im gleichen Masse zerfallen ist. Bei einer quantitativen Auswertung muss dies entweder durch eine Standardprobe ähnlicher Aktivität, deren Mutter–Tochter Trennung gleichzeitig durchgeführt wurde, berücksichtigt werden oder man wartet das Anwachsen der neuen Tochtersubstanz ab und autoradiografiert erst dann.

Zirkonium-95

Fällungsbad. Gefällt wird in einer 0.1% Lösung von *p*-Dimethylaminophenylazophenylarsinsäure in Äthanol, das 5% konzentrierte Salzsäure enthält. Zur Bildung des inaktiven Bodenkörpers wird etwas Zirkoniumoxychloridlösung zugesetzt.

Waschbad. 1 *N* Salzsäure mit inaktivem Bodenkörper der Zirkoniumfällungsform.

Bemerkung. Bei der Fällung des Zirkoniums findet eine teilweise Trennung von der Tochtersubstanz Niob statt. Das Niob wird durch die Säurebehandlung teilweise am Filter als unlösliche Niobsäure ausgefällt, zum Teil jedoch ausgewaschen. Diese Fällung tritt manchmal schon beim Lösen der Perle in Salzsäure auf. Bei einer Autoradiografie eines Ringes sieht man das Niob über die innere Ringfläche verteilt. An der Auftragstelle ist ein Punkt erhöhter Niobkonzentration, da schon im Spitzröhrchen eventuell ausgefallene Niobsäure vom Filter an der Auftragstelle festgehalten wird. Bei der quantitativen Auswertung von jungen Staubsammelproben, ist es bei geforderter Genauigkeit notwendig, bei einer Herstellung des Autoradiogramms vor Abklingen des Niobs seine Schwärzung in den Sektoren zu kennen. Diese erhält man, wenn man den entsprechenden Sektor vor der Behandlung mit Fällungsreagens halbiert und diesen als Niobsektor bestimmten Ringteil nur in dem für diesem Sektor bestimmten Waschbad badet. Dadurch werden aus diesem Sektor alle anderen Nuklide ausgewaschen und er zeigt nach der Autoradiografie nur die Niobschwärzung an, die von der gemessenen Schwärzung des Nuklids in Abzug gebracht werden kann. Eine Korrektur der Schwärzung des Zirkoniumsektors ist auf diese Weise nicht notwendig, da hier die Summe beider Schwärzungen gewünscht wird. Die Niobverluste, die die Grundschwärzung der inneren Sektorfläche bewirken geben hier einen vernachlässigbaren Fehler.

Cer-144

Fällungsbad. Gefällt wird in einer 10% Oxalsäurelösung in 0.2 *N* Salzsäure mit inaktivem Ceroxalat als Bodenkörper.

Waschbad. 0.2 *N* Salzsäure mit einem Bodenkörper von inaktivem Ceroxalat.

Bemerkung. Das Gleichgewicht Cer–Praseodym wird nicht gestört, da beide gefällt werden. Durch das gleiche chemische Verhalten erübrigt sich auch der Zusatz eines Praseodym-Trägers bei der Analyse.

Mit dem Cer fällt auch die Tochter des Strontium-90 das Yttrium-90 mit aus, was bei quantitativer Auswertung berücksichtigt werden muss oder man wartet bis das Yttrium abgeklungen ist und autoradiografiert erst dann.

Ruthenium-106

Fällungsbad. Gefällt wird in einer Ammonsulfidlösung mit inaktivem Rutheniumsulfid als Bodenkörper.

Waschbad. 1 *N* Salzsäure mit Rutheniumsulfid als Bodenkörper.

Bemerkung. Zwischen Fällungs- und Waschbad wird der Sektor in Wasser gespült.

Das Rutheniumsulfid wird aus ammoniakalischer Lösung gefällt, da es aus saurer Lösung zu langsam ausfällt und grossteils schon vor der Fällung vom Filter gelöst wird.

ÜBERPRÜFUNG DES TRENNEFFEKTS

Die Methode wurde mit Nuklidlösungen bekannter (Tabelle II) Konzentration ausgearbeitet und überprüft.

TABELLE II

Nuklid	*Konzentration ($\mu C/ml$)*	*Träger*	*Konzentration des Kation (mg/ml)*
^{137}Cs	2	Cäsiumnitrat	0.1
^{90}Sr	2	Strontiumnitrat	0.1
		Yttriumnitrat	0.1
^{95}Zr	4.5	Zirkoniumoxychlorid	0.1
^{144}Ce	0.46	Ceriammonnitrat	0.1
^{106}Ru	3	Rutheniumtrichlorid	0.17

Von jedem dieser Nuklide wurde ein Ring durch Aufbringen von 10 μl der angegebenen Nuklidlösung bereitet und jeder Ring in 6 Sektoren zerschnitten. Für jedes Nuklid wurde die Trennung, durch Baden der Sektoren in den entsprechenden Lösungen durchgeführt. Je ein Sektor eines Ringes wurde unbehandelt für Vergleichszwecke zurückgelassen. Da in jedem Ring bzw. den davon hergestellten Sektoren nur ein Nuklid vorhanden ist, soll nur in dem, für dieses Nuklid bestimmten Fällungsbad eine Fixierung dieses Nuklids durch Fällung stattfinden, während in den anderen Bädern dieses Nuklid ausgewaschen werden soll.

Bei einer 100% Fällung, wie sie durch Sättigung der Bäder mit den entsprechenden inaktiven Niederschlägen zu erwarten ist, sollten bei einer Autoradiografie die Schwärzungen der Vergleichssektoren mit den in dem entsprechenden Fällungsbad gebadeten Sektoren übereinstimmen, beziehungsweise um den Betrag verändert sein, der der unterschiedlichen Selbstabsorption durch die Veränderung der chemischen Verbindung im unbehandelten und behandelten Sektor entspricht. Die Übereinstimmung wird auch noch gestört durch die bevorzugte Laufrichtung im

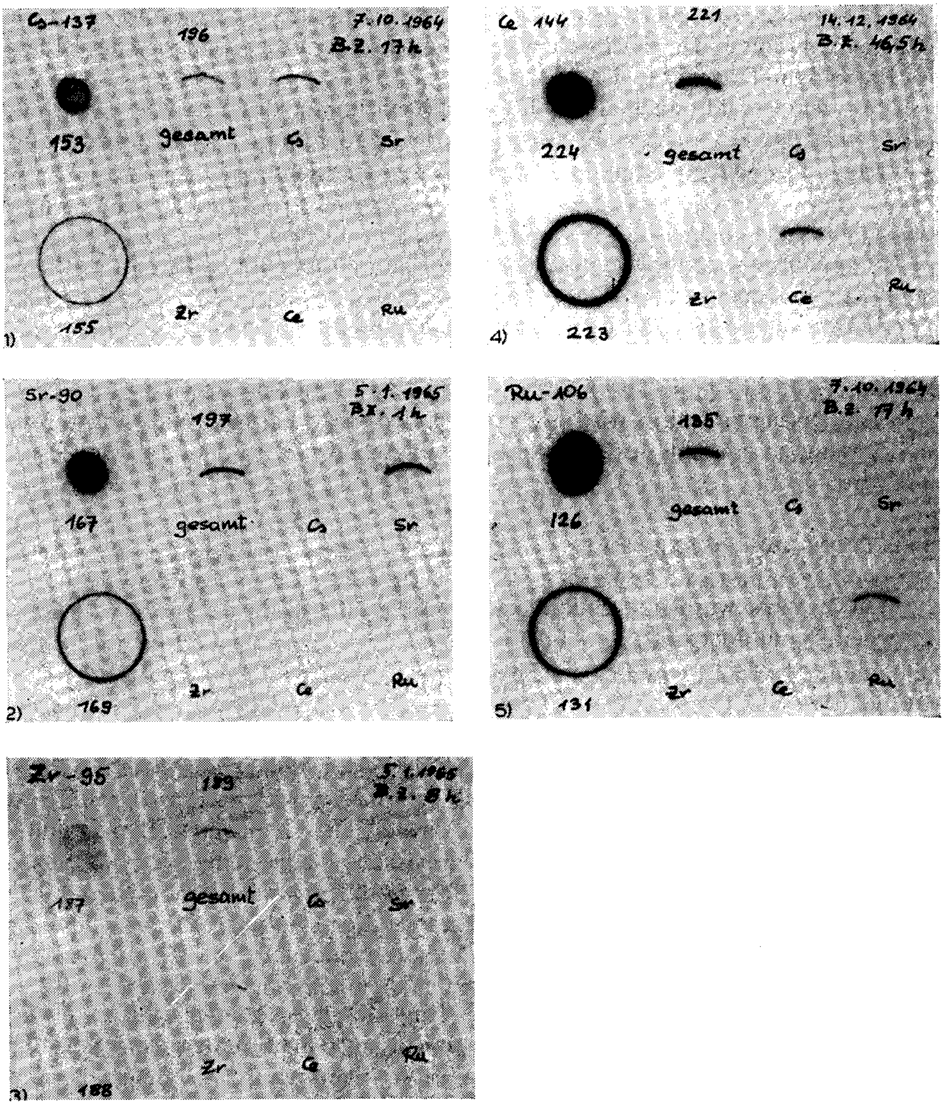

Fig. 3. Autoradiografien der Filtersektoren nach der Fällung.

Papier und die damit verbundene ungleichmässige Verteilung des Nuklids im Ring. Dieser Fehler wurde hier auf ein Mindestmass eingeschränkt durch Verwendung von 2 gegenüberliegenden Sektoren des Ringes mittlerer Aktivität für Bezugssektor und entsprechenden Nuklidsektor für die Fällung. Figur 3 zeigt die Autoradiogramme, die auf diese Weise erhalten wurden. Es wurde jeweils noch ein unbehandelter Tüpfelfleck und ein Ring des gleichen Nuklids mitautoradiografiert.

In Tabelle III sind die in den Sektorautoradiogrammen gemessenen mittleren Schwärzungswerte wiedergegeben. Sie wurden mit einem Zeiss-Schnellfotometer gemessen, unter Verwendung einer Rechteckblende von 0.5 mm Spaltbreite, auf die und deren beobachtbare Umgebung, ein 21fach vergrössertes Bild des auszuwertenden Autoradiogramms projiziert wird, wodurch die Auswertung sehr erleichtert wird. Die ausgemessene Fläche betrug im vorliegenden Fall jeweils 0.02 mm².

TABELLE III

Nuklid	*Schwärzung*		
	Grund	*Unbehandelt*	*Gefällt*
Cäsium/Barium	0.240	0.489	0.508
Strontium/Yttrium	0.308	0.966	0.956
Zirkonium/Niob	0.325	0.608	0.600
Cer/Praseodym	0.415	1.29	1.10
Ruthenium/Rhodium	0.309	0.865	0.730

Autoradiografiert wurde, ausser bei Zirkonium, nach Einstellung des neuen Gleichgewichts. Im Falle des Zirkoniums/Niob war zum Zeitpunkt der Autoradiografie das Niob, das in den anderen Sektoren durch Säurefällung zum Teil fixiert wurde, erst auf 15% seiner Aktivität abgeklungen. Diese Sektoren weisen eine Schwärzung von 0.390 auf, die sich aber von der Grundschwärzung zu schwach abhebt, um in der Bildreproduktion wiedergegeben zu werden. Im gefällten Zirkoniumsektor war das Gleichgewicht, da das Niob hier natürlich ebenso gefällt wurde, nicht erheblich gestört. Der Trenneffekt und die Wiederauffindung des Nuklids in dem dafür bestimmten Sektor, ist in allen Fällen durch das nachgeschaltete Waschbad zufriedenstellend gelöst. Die Wiederauffindung des Nuklids nach durchgeführter Fällung ist bei Cäsium, Strontium und Zirkonium vollkommen, bei Cer und Ruthenium etwas schlechter. Dieser Verlust lässt sich nicht durch die Änderung der Selbstabsorption erklären. Der Verlust dürfte auf eine verzögerte Fällung und Auswaschung zurückzuführen sein. Bei einer quantitativen Auswertung wird dieser Fehler durch einen gleichbehandelten Standardring kompensiert. Bei quantitativer Auswertung von Autoradiogrammen ist es bei den Nukliden, wo eine Mutter–Tochter Trennung vollkommen (Strontium–Yttrium) oder teilweise (Zirkonium–Niob) auftritt bei langen Halbwertszeiten nicht notwendig auf das Einstellen des neuen Gleichgewichts nach durchgeführter Trennung zu warten, sondern es genügt ein Vergleichsautoradiogramm ungefähr gleicher aber bekannter Konzentration, wie die Probe und unter den selben zeitlichen Bedingungen autoradiografiert, für die Auswertung zur Verfügung zu haben.

Eine rechnerische Erfassung des Anwachsens der neuen Tochter in Bezug auf die Schwärzung ist nicht möglich, da die Schwärzung nicht nur von der Konzentration und Expositionszeit, sondern auch von den Strahlungsenergien abhängig ist und sowohl Mutter als auch Tochter unter Aussendung mehrerer Strahlungen verschiedener Energie zerfallen.

Zur Bestimmung des Fehlers, der bei der quantitativen Auswertung aller Sektoren eines Ringes durch die ungleichmässige Substanzverteilung im maschingemachten Papier auftritt, wurden radioaktive Ringe in 6 Sektoren zerschnitten und einzeln unter dem Endfensterzählrohr gemessen. Aus diesen Werten wurde die dreifache Standardabweichung, die einen Vertrauensbereich von 99.7% einschliesst ermittelt und daraus die Varianz berechnet. Als maximaler Wert der Varianz wurde 22.8% erhalten. Daraus ist der grosse Fehler, der in der Verwendung eines maschinell erzeugten Papieres liegt zu ersehen. Unterschiedliche Werte der Varianz wurden erhalten, da die Standardabweichung eines Ringes vom Zerschneiden des Ringes abhängt, ob und wie die Pole stärkster Aktivität geteilt werden.

Analyse einer Staubasche

Für eine Staubanalyse standen Staubsammelfilter, die schon weitgehend abgeklungen waren, und eine Staubasche aus eben dieser Zeit (1961 bis 1962) zur Verfügung. Für die Erprobung der Methode wurde die Staubasche gewählt, die unter den gleichen Bedingungen wie ein Staubsammelfilter verarbeitet wurde. Die Aktivitätsmessung der Staubasche ergab, unter dem Glockenzählrohr gemessen und auf Kaliumchlorid bezogen

am 25.10.1962	$24.3 \cdot 10^{-12}$ Curie/mg
am 14.10.1964	$11.8 \cdot 10^{-12}$ Curie/mg

Am 24.7.1964 wurde versucht von 20 mg dieser Asche ein γ-Spektrum aufzunehmen*. Dies geschah auf einem "Intertechnique" 400 Kanal Impulshöhenanalysator mit einem 3 x 3 Zoll Harshaw NaJ (Tl) Kristall. Es wurde zuerst der Leerwert und dann die Probe je 15 Stunden eingespeichert und dann die beiden Spektren ausgedruckt. Das Staubspektrum war gleich dem des Leerwertes und es konnte keinerlei Aussage auf ein vorhandenes Nuklid gemacht werden.

1.7 Milligramm Staubasche, entsprechend $20.1 \cdot 10^{-12}$ Curie, das entspricht der während der Messperiode 1961/62 schon oft registrierten Gesamtaktivität (langlebige Aktivität) eines einzelnen Luftfilters, wurden auf ein leeres Staubsammelfilter verrieben, um ähnliche Ausgangsbedingungen geschaffen zu haben, wie sie bei der Veraschung eines Staubsammelfilters gegeben sind. Dieses Filter wurde sodann auf die schon erwähnte Weise verascht und die Staubasche dabei gleichzeitig in einer Borax–Soda Perle aufgeschlossen. Nach Anreicherung am Filter im Ring, wurde das Filter in 6 Sektoren zerschnitten und nach durchgeführter Trennung autoradiografiert. Figur 4 zeigt das für die Autoradiografie vorbereitete Filter und ein Autoradiogramm, das nach einer Expositionszeit von 30 Tagen erhalten wurde. Mit dem Zeiss-Schnellfotometer wurden dazu folgende Schwärzungswerte gemessen:

Grundschwärzung des Films	0.476
Unbehandelter Vergleichssektor	1.33
Cäsium	0.860
Grundschwärzung zu Cäsium	0.715
Strontium	0.742
Ruthenium	0.660

Es liessen sich also in 1.7 mg Staubasche, die *ca.* im Mittel hinsichtlich ihres Staubes 2.5 Jahre alt war, Cäsium, Strontium und Ruthenium nachweisen. Zirkonium mit seiner relativ kurzen Halbwertszeit von 65 Tagen ist natürlich schon abgeklungen. Cer ist soweit abgeklungen, dass es nicht mehr nachgewiesen werden konnte.

Die hohe Grundschwärzung des Cäsium-Sektors ist dadurch begründet, dass die Platinchlorwasserstoffsäure nach jeder Operation wieder aufgehoben wurde (es standen nur 25 ml zur Verfügung). Durch die zahlreichen Versuche reicherte sich in der Lösung, durch Auswaschen anderer Nuklide die Aktivität sehr an. Diese, an den

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* Für die Durchführung der γ-spektrometrischen Untersuchung und für die Bereitstellung aller verwendeten Nuklidlösungen danken wir Herrn Dr. H. SORANTIN, Reaktorzentrum Seibersdorf, recht herzlich.

Bodenkörper absorbiert, lagerte sich am Filter ab und wurde im anschliessenden Waschbad nicht mehr vollständig entfernt. Diese geringen, anhaftenden Aktivitäten geben dann diesem Sektor bei langen Expositionszeiten in der Autoradiografie die hohe Grundschwärzung. Bei einer Auswertung muss man sie natürlich von der Ringschwärzung subtrahieren.

Die gebrauchten Bäder der anderen Nuklidfällungen, wobei jeweils 10 ml verwendet wurden, wurden nur einmal verwendet.

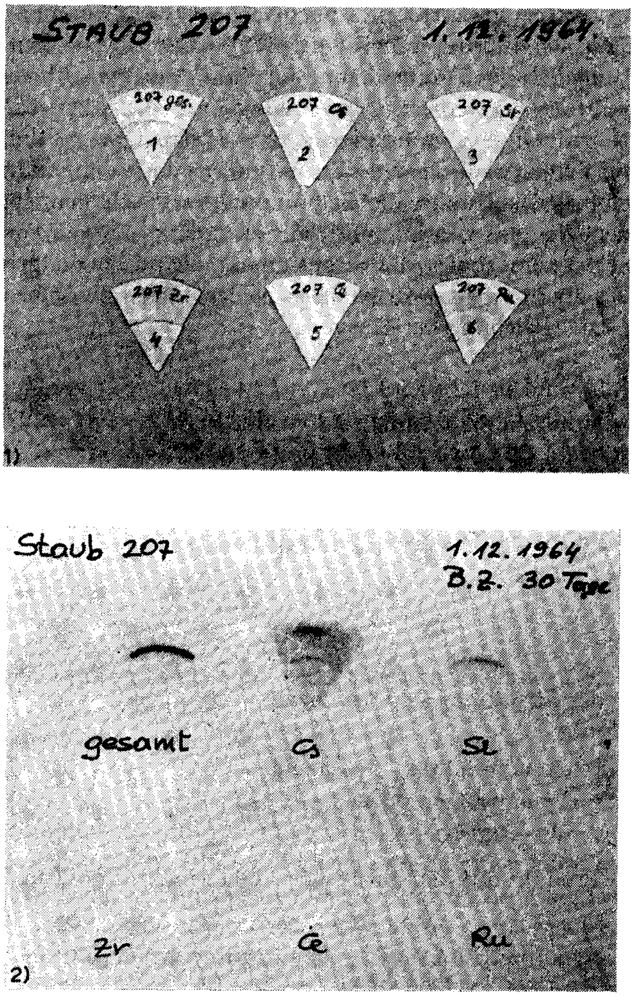

Fig. 4. Trennung der Nuklide einer Staubsammelprobe.

QUANTITATIVE AUSWERTUNG

Hätte man von jedem Radionuklid einen kompletten Ring zur Verfügung, was einfach durchzuführen wäre, aber die Empfindlichkeit des Verfahrens um das Sechsfache vermindern würde, könnte eine quantitative Auswertung durch Chronoautoradiografie erfolgen[8]. Die Auswertung dieser Autoradiogramme erfolgt visuell und beruht auf dem Vergleich von Schwärzungen gleichen Intensität. Die Ermittlung der gesuchten Aktivität wird mittels des Reziprozitätsgesetzes durch Gleichsetzen der Produkte von spezifischer Flächenaktivität und Expositionszeit für Probe und Standard durchgeführt.

Das Reziprozitätsgesetz, das bei der Autoradiografie auch für Extremfälle erfüllt ist[14] besagt, dass bei gleicher Schwärzung das Produkt aus spezifischer Flächenaktivität und Expositionszeit gleichgesetzt werden darf. Im vorliegenden Fall ist eine instrumentelle Auswertung vorzuziehen, wobei eine direkte Bestimmung der spezifischen Dosis, also die in der Flächeneinheit enthaltene Aktivität, aus dem gemessenen Schwärzungswert möglich ist. Voraussetzung für diese Auswertmethode ist jedoch die Kenntnis der Funktion, durch die die Schwärzung S und die spezifische Dosis E miteinander verknüpft sind. Diese Schwärzungskurve ist abhängig vom Film, den Entwicklungsbedingungen, der Exposition und der Art und Energie der Strahlung. Es ist also notwendig für jedes Nuklid die Schwärzungskurve zu kennen. Ottendorfer[15] beschrieb einen Weg zur Bestimmung der Schwärzungskurven von Nukliden. Er berechnete die Schwärzungskurve des Strontium-90, die für die quantitative Auswertung unverändert übernommen wurde, da in beiden Fällen die selben Arbeitsbedingungen vorlagen. Die Gleichung der Kurve lautet:

$$\log E = 1.1998 \cdot \log S + 0.98819$$

Für den Standardsektor mit bekanntem Strontiumgehalt ergibt sich:

Gemessene Schwärzung des Strontium-Sektors	0.956
Grundschwärzung des Films	0.308
Wahre Schwärzung des Strontium-Sektors	0.648

$$\log E = 1.1998 \cdot \log 0.648 + 0.9882$$
$$E = 5.784$$

Für die Probe gilt:

Gemessene Schwärzung des Strontium-Sektors	0.742
Grundschwärzung des Films	0.476
Wahre Schwärzung des Strontium-Sektors	0.266

$$\log E = 1.1998 \cdot (0.4249 - 1) + 0.9882 = 0.2982$$
$$E = 1.987$$

Die spezifische Dosis E ist das Produkt aus der spezifischen Flächenaktivität I und der Expositionszeit t

$$E = I \cdot t$$

wobei I die in der Flächeneinheit enthaltene Aktivität angibt. Für den Standardring wurden 10 μl einer Lösung von 2 μC/ml verwendet. Demnach waren im Standardring $2 \cdot 10^{-8}$ Curie Strontium-90, die nach einer Stunde Expositionszeit die angegebene Schwärzung ergaben. Die Fläche des Ringes darf in beiden Fällen gleichgesetzt werden. Die Aktivität des gesuchten Strontium-90 ergibt sich aus folgender Proportion:

$$Akt_{\mathrm{St}} \cdot Exp.Z._{\mathrm{St}} : E_{\mathrm{St}} = Akt_{\mathrm{P}} \cdot Exp.Z._{\mathrm{P}} : E_{\mathrm{P}}$$

Die Expositionszeit des Proben-Sektors betrug 1 Monat, das sind 720 Stunden

$$2 \cdot 10^{-8} \cdot 1 : 5.784 = x \cdot 720 : 1.987$$
$$x = 9.54 \cdot 10^{-12}$$

Die Aktivität des Strontium-90 betrug somit *9.54 ·10⁻¹² Curie*.
Daraus ergibt sich die Aktivität des Strontium-90 zum Zeitpunkt der Analyse in *1 mg Staubasche* mit *5.62 ·10⁻¹² Curie* oder, da die Gesamtaktivität der Asche $11.8 \cdot 10^{-12}$ C/mg betrug, ein Aktivitätsanteil des Strontium-90 mit *47.6%*.

Es lässt sich ein Rückschluss für den Zeitpunkt der Staubsammlung ziehen, wie hoch der Aktivitätsanteil des Strontium-90 gewesen ist. Die Staubasche wurde aus einem Staub einer mehrmonatigen Sammelzeit gewonnen. Die Berechnung wurde auf die Zeit Mitte 1962 bezogen und dem Aktivitätswert der Asche bei ihrer Herstellung gegenübergestellt. Dieses Ergebnis gibt nur einen annähernden Wert über den Aktivitätsanteil des Strontium im gesammelten Staub, da die Asche aus einer längeren Sammelzeit entstammt und bei ihrer Aktivitätsbestimmung die Nuklide entsprechend ihren Sammelzeitpunkten und Halbwertszeiten abgeklungen sind.

Die Berechnung der Strontiumsaktivität auf einen Zeitpunkt vor 2.5 Jahren mittels des radioaktiven Zerfallgesetzes ergibt:

$$A_0 = 10.15 \cdot 10^{-12} \text{ Curie}$$

1.7 mg Asche hätte $10.15 \cdot 10^{-12}$ Curie Strontium aufgewiesen, das sind $5.97 \cdot 10^{-12}$ C/mg. Das ergibt für das *Strontium-90* einen Aktivitätsanteil von 24.6%.

Die eingesetzte Staubasche für den Aufschluss entspricht der Menge, die von $1.7/0.221 = 7.7$ Filtern durch Veraschen erhalten wurde. Bei einem mittleren Durchsatz von 4.5 m³ Luft pro Filter wäre das der Staub aus 34.7 m³ Luft.

Die Strontiumaktivität auf 1 m³ Luft berechnet sich zu

$$\frac{10.15 \cdot 10^{-12}}{34.7} = 2.92 \cdot 10^{-13} \text{ C/m}^3\text{, das sind}$$

drei Zehnerpotenzen unter der maximal zulässigen Konzentration.

DISKUSSION

Die beschriebene Methode gestattet eine Trennung und quantitative Bestimmung des aus 35 m³ Luft erhaltenen Staubes hinsichtlich der langlebigen Nuklide durchzuführen. Die Staubmenge, die in einer Perle aufgeschlossen werden kann ist etwa 8 mg, entsprechend 1–2 mg Staubasche. Bei einer Strontium-Aktivität, die um *drei Zehnerpotenzen* unter der maximal zulässigen Konzentration liegt, ist eine quantitative Auswertung nach 30 Tagen Expositionszeit möglich.

Bei einem Einsatz dieser Methode in Katastrophenfällen, bei Erreichung der maximal zulässigen Konzentration, lässt sich eine quantitative Bestimmung der Nuklide im Staub insgesamt in rund 2.5 Stunden durchführen, da dann für die Exposition 45 Minuten ausreichend sind.

Somit kann dieses Verfahren mit der γ-Spektrometrie konkurrieren, da noch dazu über das Strontium-90, das gefährlichste langlebige Nuklid, eine quantitative Aussage gemacht werden kann.

Einen besonderen Vorteil aber bietet sie dann, wenn die Art der geforderten

Bestimmung, die Gewinnung einer grösseren Probemenge bzw. einer Probe genügend hoher Aktivität auf Schwierigkeiten stösst. Solche Probleme können bei der analytischen Bestimmung von Radionukliden in Staubproben, in natürlichen Gewässern oder Abwässern oder in Mineralien auftreten. Die Methode bietet auch dort Vorteile, wo bei höheren Aktivitäten eine instrumentelle Methode versagt, da hier eine Analyse und Bestimmung für Strahler jeder Strahlungsart in tragbarer Zeit möglich ist. Der Arbeitsaufwand für den Aufschluss der radioaktiven Probe, Anreicherung im Ring und selektive Fällung beträgt bis zu der, für eine Autoradiografie bereiten Probe nur maximal 45 Minuten. Die Zeit für die Autoradiografie richtet sich nach der Aktivität der Probe.

Aber auch in Kombination mit einer instrumentellen Methode bringt sie Vorteile, wie z.b. durch Vortrennung einer Probe für eine Auswertung in einem Impulshöhenanalysator, wenn bei überdeckten Maxima keine eindeutige Zuordnung auf ein vorhandenes Nuklid getroffen werden kann.

Bei der Ausarbeitung wurde auf eine einfache und billige Durchführung Rücksicht genommen. Für eine qualitative Aussage ist an Geräten nur eine elektrisch beheizbare Platindrahtspirale, ein Ringofen und einiges Kleinmaterial (Reagenzien, Filmmaterial, ev. Trockenlampe usw.) notwendig. Eine quantitative Auswertung eines Autoradiogramms lässt sich ohne Verwendung eines Fotometers mit gleicher Genauigkeit[8] durch visuelle Zuordnung gleicher Schwärzung zu einer Standardskala durchführen.

Durch die einfache Durchführung lässt sich die Methode speziell als Feldmethode einsetzen, um gefordertenfalls am Ort der Probennahme die Analysen durchzuführen.

ZUSAMMENFASSUNG

Es wurde ein mikrochemischer qualitativer und quantitativer Trennungsgang für langlebige Radionuklide der Uranspaltung (Cs, Sr, Ce, Zr, Ru) in Staubproben beschrieben: Das beladene Staubsammelfilter wird mit Trägerlösung und einer Lösung des Aufschlussmittels angefeuchtet und in einer elektrisch regelbar heizbaren Platinspirale verascht, wobei der Staub in der sich bildenden Schmelzperle im selben Arbeitsgang aufgeschlossen wird. Die Lösung der in verdünnter Säure gelösten Perle wird am Ringofen in einen Ring konzentriert, das Papier mit dem radioaktiven Ring in Sektoren zerschnitten und für jedes Nuklid auf einem Sektor eine spezifische Fällungsreaktion durchgeführt. Die Identifizierung und quantitative Auswertung erfolgt nach Autoradiografie der Sektoren. Die praktische Erprobung wurde mit einer 2.5 Jahre alten Staubprobe, herrührend aus den Kernwaffenversuchen in den Jahren 1961 bis 1962 durchgeführt, wobei in 1.7 mg Staubasche radioaktives Cäsium, Strontium und Ruthenium nachgewiesen wurden. Die quantitative Auswertung des Strontium-90, das in der Grössenordnung von 10^{-12} Curie lag, zeigte die Empfindlichkeit des Verfahrens. Auf den Anwendungsbereich des beschriebenen Verfahrens wurde hingewiesen.

SUMMARY

A microchemical qualitative and quantitative separation process for long-lived radionuclides from uranium fission (Cs, Sr, Ce, Zr, Ru) in dust samples is described. The loaded dust filter is moistened with carrier solution and with borax–sodium carbonate, and ashed in an electrically heated platinum spiral; the dust is thus decomposed, forming beads. The solution of the bead in dilute acid is concentrated in a ring with the ring oven; the paper bearing the radioactive ring is cut into sectors and a specific precipitation reaction is applied for each nuclide in separate sectors. Identification and determination are carried out by autoradiography of the sectors. Practical testing was done with a 2.5-year old dust sample originating from nuclear studies in 1961–62; radioactive Cs, Sr and Ru were detected in 1.7 mg of dust ash. The quantitative evaluation of strontium-90 of the order of 10^{-12} C showed the sensitivity of the method. The range of application of the method is indicated.

RÉSUMÉ

On décrit une méthode de séparation microchimique qualitative et quantitative de poussières de radionucléides de longue période (Cs, Sr, Ce, Zr, Ru) provenant de la fission de l'uranium. Le filtre chargé de la poussière est préparé et inciné dans une spirale de platine, chauffée électriquement; la poussière se transforme en perles. Après dissolution, on concentre en un anneau. Le papier supportant l'anneau radioactif est coupé en secteurs: une réaction de précipitation spécifique est appliquée pour chaque nucléide dans les secteurs séparés. Identification et dosage sont effectués par autoradiographie des secteurs.

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DIRECT SPECTROGRAPHIC DETERMINATION OF IMPURITIES IN URANIUM TETRAFLUORIDE

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Uranium tetrafluoride is an important intermediate product in the production or regeneration of uranium reactor fuels. Reactor materials must be extremely pure, the permissible impurities lying at the p.p.m. or even p.p.b. level, and spectrochemical methods are most suitable for the determination of such low quantities. Emission spectroscopy generally gives satisfactory results in the shortest time with the smallest consumption of sample.

There is little information on the spectrographic analysis of uranium tetrafluoride in the literature. The procedures are generally indirect and based on prior pyrohydrolysis of UF_4 to form UO_2[1-3]. This chemical treatment procedure possesses disadvantages in an increased time of analysis and the possibility of contamination of the sample; moreover, elements which form volatile fluorides can be lost during pyrohydrolysis. However, direct qualitative or quantitative spectrographic analysis of UF_4 is not possible; because of the great volatility of the compound, uranium gives very complex spectra, and there is a high background.

It is clear that direct spectrographic analysis of uranium tetrafluoride would be possible, if escape of UF_4 from the electrode, and its volatilisation into the arc column could be prevented. More strictly, the impurities in UF_4 could be determined, if UF_4 were converted to refractory UO_2 in the electrode cavity itself. An approach to this problem was made by ATWELL AND HELLER[4]: by the action of lithium metasilicate, UF_4 was transformed to UO_2 and the very volatile SiF_4, which causes no spectrographic difficulties. The method was applied to analysis of molybdenum and vanadium in UF_4. Lithium served as a spectrographic buffer. The merit of the procedure is very dependent on the suppressor preparation and on the composition of the sample-suppressor mixture.

In previous work[5] and in the present work, attempts were made to find a suppressor, which would give good results for the determination of a larger number of elements and would also have a minimal influence on the excitation conditions. Various alkali silicates, boric acid, silica, alumina and indium oxide were examined. Alumina was found to be the best suppressor, because its spectrum is poor and easily detected. Moreover, aluminum fluoride is of medium volatility, so that it evaporates smoothly from the electrodes. Alumina does not lower the intensity of the spectra of other elements and the compound is refractory, so that melts are not formed in the electrode. Indium oxide has similar properties except for its greater influence on the emission of other elements.

EXPERIMENTAL

The experimental parameters are given in Table I, and the dimensions and arrangement of the electrodes are shown in Figs. 1 and 2.

TABLE I

EXPERIMENTAL CONDITIONS

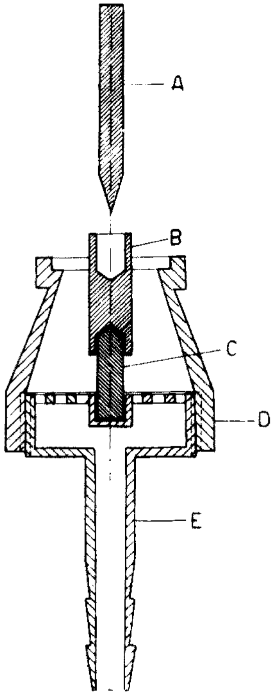
Spectrograph:	Large Littrow type, quartz optics, Hilger E 478.
Spectral range:	2450–3550 Å.
Slit:	20 μ wide, 2 mm high.
Illumination:	Spherical lens Hilger F 1025.
Atmosphere:	Oxygen 150 l/h, argon 600 l/h, gas sheath as in Fig. 1.
Electrodes:	Johnson–Matthey 2B, cathode (Fig. 1A, 2A), anode (Fig. 1B, 2B), supporting electrode (Fig. 1C, 2C).
Electrode gap:	4 mm.
Excitation:	D.C. arc of 8.5 A (Hilger BNF Source Unit FS 131).
Exposure:	prearc: none, arc : 60 sec.
Plate:	Ilford Ordinary N.30.
Plate processing:	Developer ID-2, 2 min, 15 sec at 18°, fixing 15 min, washing 15 min.
Microphotometer:	Recording microphotometer Hilger 451.
Plate calibration:	7-step neutral filter, 6-A iron arc D.C., prearc 5 sec, arc 25 sec.
Calculations of log. intensity ratios:	Respectra calculator, Dennert & Pape, Hamburg.
Analytical pairs:	see below
Suppressor:	Al_2O_3 (specpure, Johnson and Matthey) +50 p.p.m. Ge in the form of GeO_2.

Analytical pairs:

Element	Internal standard
B 2497.7	Ge 2592.5
Mo 3132.6	Al 3059.9
V 3184.0	Al 3059.9
Co 3405.1	Al 3059.9
Ti 3371.5	Al 3059.9

Procedure

Weigh 50 mg of sample, previously dried at 100° for 3 h, into the cavity of the graphite electrode. Pour 25 mg of alumina, containing the internal standard element, over the sample. Cautiously press down with a hand press. Two layers are formed in the cavity: the upper alumina, and the lower sample. Arrange the electrode on the supporting electrode as shown in Fig. 1. The d.c. arc is struck against the upper graphite electrode after the electrode gap has been flushed for 30 sec with the atmosphere of argon and oxygen. Develop the spectrographic plates under controlled conditions and calibrate with the iron arc. Measure the densities of the analytical and internal standard lines with a microphotometer. The same procedure is carried out with standard samples of UF_4. The logarithms of the intensity ratios were calculated with a "Respectra" calculator, and plotted against the logarithms of the concentrations to obtain working curves.



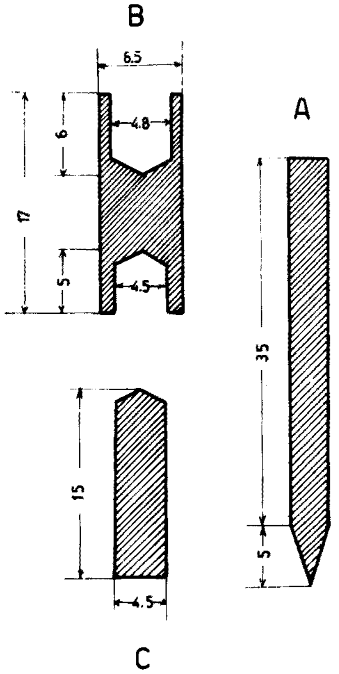


Fig. 1. Arrangement of electrodes in gas sheath device.

Fig. 2. Dimensions of graphite electrodes used.

Standards

Standards for the evaluation of the analytical results were prepared from pure UF_4 with the additions of oxides of the elements to be determined. Normally, 4 elements were present in one standard. To prevent contamination of the samples from the corrosive action of fluorides on agate or other materials, the mixtures were prepared by mixing in a plexiglas mortar. The stock mixture contained 20,000 p.p.m. of the element. Dilute mixtures were prepared by proper dilution with UF_4 and contained 1000, 500, 100, 50, 25, 10, 5 and 1 p.p.m. of the element. All the samples were kept in polyethylene bottles. Mixing was carried out in glove-boxes, because of health hazards.

Very pure UF_4 was synthetized by the following procedure. Uranium(IV) was obtained by reduction with hydrogen of a uranyl nitrate solution of high purity, using platinum as a catalyst. The reduction proceeded slowly, and 50 g of uranyl nitrate were satisfactorily reduced in 20 h. Platinum was filtered off and the uranium(IV) was precipitated with hydrofluoric acid in a polyethylene beaker. The product was filtered and dried to constant weight at 100°. (Moisture must not be present, because moist samples are blown off the electrode.) At higher temperatures, UF_4 undergoes a slight decomposition[6]. Owing to the impurities in the chemicals (especially in hydrofluoric acid), the product normally contained traces of Fe, Si, Mg, Ca and Pb.

DISCUSSION

Alumina as the suppressor

From a study of the influence of various amounts of alumina on the suppression of uranium excitation, it was concluded that the minimal quantity, which gave the best results, was 25 mg of alumina, when 50 mg of uranium tetrafluoride were taken. Smaller amounts caused higher backgrounds whereas higher amounts did not improve the clarity of the spectrogram. To avoid higher dilutions of the sample, 25 mg of alumina were chosen as a constant amount. Previously[5], homogeneous mixtures of UF_4 and alumina were studied. The spectra obtained for such mixtures could be used up to 2850 Å, but beyond this range the uranium background became too high for quantitative measurements.

It is known that the majority of spectral lines of most elements can be found in the spectral region up to 3500 Å, where CN-bands begin to appear. Some experiments were done to extend the usefulness of the alumina procedure to this region. The reactions in the electrode were provisionally visualized as follows: due to the high temperature in the electrode, UF_4 decomposes and volatilizes into the arc gap. Meanwhile, it can react with other particles (namely, alumina) and fluorinate them[7] while itself being converted to the refractory oxide. The possibility of reaction increases with the number of alumina particles. A layer of alumina is obviously best, for all the particles of UF_4 during escape must traverse this layer, giving a maximal chance of reaction.

This assumption of the electrode reactions was experimentally verified: when an alumina layer was used instead of the previous homogeneous mixture, the spectrograms were clear up to 3500 Å, indicating minimal amounts of uranium in the arc column. (The suppressing effect of alumina is demonstrated in Figs. 3 and 4.)

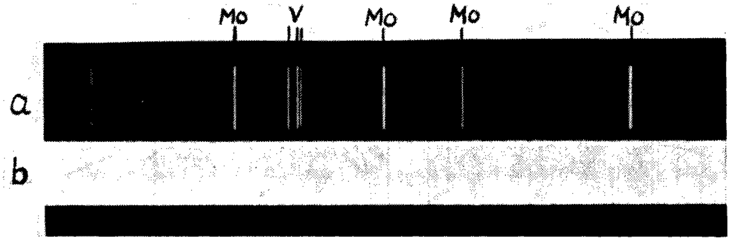


Fig. 3. The spectra of the sample containing 50 p.p.m. of vanadium and molybdenum in UF_4. (a) with Al_2O_3 suppressor present; (b) without Al_2O_3.

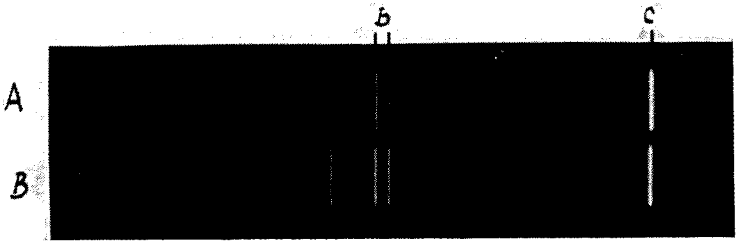


Fig. 4. The spectra of the sample containing 10 p.p.m. of boron in UF_4. (a) with Al_2O_3; (b) without Al_2O_3.

The physical appearance of alumina was of great importance: it must be neither too plastic nor too powdery. In both cases, the hot gases blow out the sample. The particle size of the alumina used in the present work was 0.07 μ.

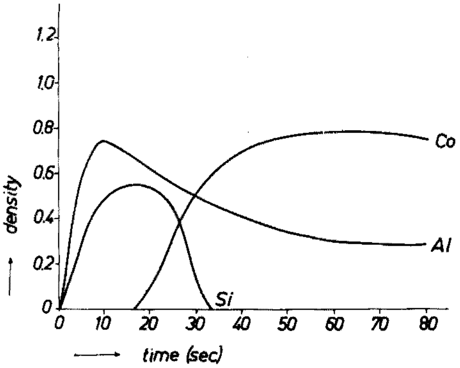
The controlled atmosphere in the excitation of spectra

When the exposures were made in air, the arc stability was poor. Some spectrographic buffers were tested to stabilize the discharge. When alkali salts were added, the stability was improved, but the intensity of the lines was reduced. Graphite produced too high a temperature in the electrode and the escape of uranium began very quickly.

A constant gas flow is known[8,9] to stabilize the discharge. A gas sheath device was adapted, which allowed simple work in controlled atmosphere (Figs. 1 and 2)[9]. With this device a great stability of the arc was achieved and the addition of the buffers was no longer necessary. The optimal flow rates of oxygen and argon were found to be 150 l/h and 600 l/h, respectively. With greater flow rates of oxygen, the temperature of the electrode rose, and uranium excitation also increased. When less oxygen was used, the background of the spectrograms was lower, but owing to the fall of the temperature, the line intensities were reduced. To remove all air from the surroundings of the electrode, the gases were allowed to flow for 30 sec before the exposure began.

The arc and the exposure

High excitation currents caused the excitation of uranium, but on the other hand too low currents decreased the excitation of impurity elements. Therefore, 8.5 A was chosen as the optimal current intensity. The time of exposure was obtained on the basis of the volatility curves, made by moving-plate spectrograms (Figs. 5–8).



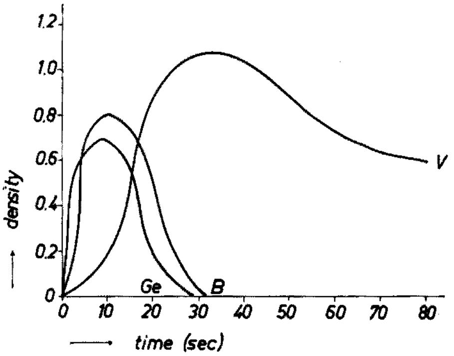
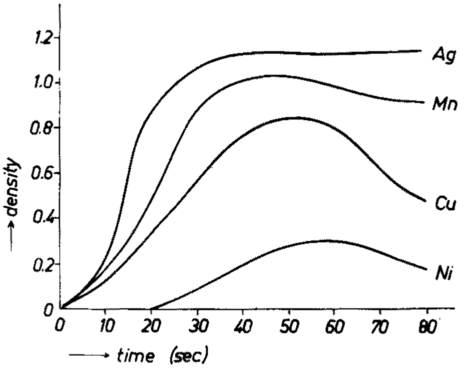


Fig. 5. Volatility curves of Si, Co and Al.

Fig. 6. Volatility curves of Ge, B and V.

From these it was concluded, that the elements could be divided into two categories, according to their volatility: elements which volatilize in a short time (B, Ge, Si), and elements which require a longer time (Mo, V, Co, etc.). The times of volatilization are influenced by the boiling points of metal fluorides. Owing to very low volatility of the fluorides of Ca, Pb, Mg, Ni, etc., these elements cannot be determined. Uranium began to volatilize 70–80 sec after the arc was struck.

The discharge process was very similar to that of the carrier distillation procedure[1]. In the initial 10 sec the electrodes warmed up, and the current was slightly lower (8 A); then burning was steady up to 70–80 sec, when the arc became unstable because of the uranium escape.



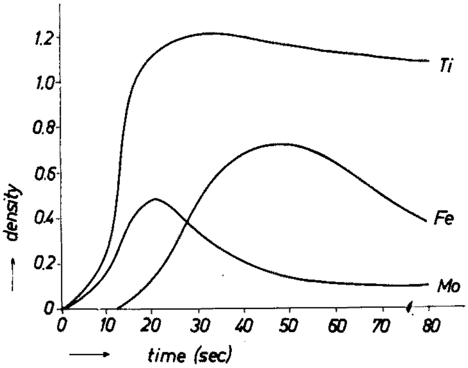


Fig. 7. Volatility curves of Ag, Mn, Cu and Ni.

Fig. 8. Volatility curves of Fe, Ti and Mo.

The internal standards

In the procedure the internal standard method was used. Because of the different volatilities of the metal fluorides, two internal standards were employed; for the elements of high volatility germanium was used, and for those of medium volatility aluminum was used. A concentration of 50 p.p.m. of germanium (as GeO_2) in Al_2O_3 produced a satisfactory intensity of the Ge 2592.5 Å line, whereas the Ge 2497.9 Å line, which can interfere with the 2497.7 Å boron line, was not visible.

Aluminum spectra are composed of few and strong lines. The only line of proper intensity, which could be used as the internal standard, was the Al 3059.9 Å line.

RESULTS

From the above discussion it can be concluded that all the trace impurities could not be determined with equal success. The most volatile elements were very sensitive, while the less volatile elements had very poor limits of detection.

The elements were treated quantitatively only in some cases; in the other cases only qualitative observations were made. The results for the behaviour of particular elements are given in Table II, while the corresponding volatility curves, which characterize the behaviour of the elements in the arc, are shown in Figs. 5–8. Of course, the quantitative results are principally general conclusions, since the procedure must be adapted to suit the experimental conditions of other workers. The general method has the advantage that the pyrohydrolysis procedure can be eliminated, and that the possible loss of impurities during chemical pretreatment of samples can be avoided.

TABLE II

THE CHARACTERISTICS OF THE ELEMENTS ANALYSED IN UF_4 BY DIRECT ARCING WITH Al_2O_3 AS A SUPPRESSOR

Element	*Spectral line (Å)*	*Volatility*	*Sensitivity (p.p.m.)*	*Reproducibility at 25 p.p.m. (%)*	*Concentration range (p.p.m.)*
Ag	3280.7	Medium	0.5	—	—
B[a]	2497.7	High	0.5	± 8	1–100
Co[b]	3405.1	Medium	5	±25	10–100
Cu	3247.5	Medium	5	—	—
Fe[c]	2488.1	Medium	10	—	—
Mn[b]	2801.0	Medium	1	±15	5– 50
Mo[b]	3132.6	Medium	0.5	±12	1–100
Nb	3195.0	Medium	40	—	—
Ni	3414.8	Very low	100	—	—
Si	2516.1	High	2	—	—
Ti[b]	3371.5	Medium	10	±18	25–500
V[b]	3184.0	Medium	1	±25	5–100
W	2947.0	Medium	40	—	—
Zr	3438.2	Medium	40	—	—

[a] Ge 2592.5 line as internal standard.
[b] Al 3059.9 line as internal standard.
[c] Fe was present in blank standards.

SUMMARY

A direct spectrographic method for the determination of some impurities in UF_4 is described. The sample in the graphite electrode was covered with a layer of alumina before the arc was struck; alumina prevents the volatilization of UF_4 and thus avoids high spectral and background interferences. To stabilize the discharge, a controlled atmosphere of argon and oxygen was used. The impurity elements were divided into 3 categories according to their volatility: high (B, Si), medium (Co, Mn, V, Mo, Ti, etc.), and low (Ni, Pb, alkaline earths, etc.). Impurities of high and medium volatility could be determined with germanium or aluminum as internal standard. The sensitivities found for this method generally agreed with those of the carrier distillation method. The coefficients of variation varied from 8 to 25% at the 25 p.p.m. level.

RÉSUMÉ

Une méthode spectrographique directe est décrite pour le dosage de quelques impuretés dans UF_4. L'échantillon dans l'électrode de graphite est recouvert d'une couche d'alumine, empêchant la volatilisation de UF_4 et ainsi évitant des interférences. Les impuretés sont divisées en 3 groupes, suivant leur volatilité: élevée (B, Si), moyenne (Co, Mn, V, Mo, Ti, etc.) et faible (Ni, Pb, alcalino-terreux, etc.). Les coefficients de variation sont compris entre 8 et 25% pour des teneurs de 25 p.p.m.

ZUSAMMENFASSUNG

Es wird eine direkte spektrographische Methode zur Bestimmung einiger

Verunreinigungen in UF_4 beschrieben. Die Probe wird in der Graphitelektrode vorher mit einer Schicht von Aluminiumoxid bedeckt. Das Aluminiumoxid verhindert die Verflüchtigung des UF_4 und vermeidet so Störungen durch zu hohen Untergrund. Um die Entladung zu stabilisieren, wird in einer Atmosphäre von Argon und Sauerstoff gearbeitet. Die Verunreinigungen werden entsprechend ihrer Flüchtigkeit in 3 Kategorien eingeteilt: hoch (B, Si), mittel (Co, Mn, V, Mo, Ti, usw.) und niedrig (Ni, Pb, Erdalkalien, usw.). Die Verunreinigungen mit hoher und mittlerer Flüchtigkeit konnten mit Germanium oder Aluminium als inneren Standard bestimmt werden. Die Empfindlichkeiten, die mit dieser Methode gefunden wurden, stimmen mit denen, wie man sie von der Trägerdestillation kennt, überein. Die Variationskoeffizienten liegen zwischen 8 und 25% bei Gehalten von 25 p.p.m.

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SPECTROPHOTOMETRIC DETERMINATION OF MOLYBDENUM IN STEEL, TANTALUM, NIOBIUM OR TUNGSTEN

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One of the best methods for the determination of traces of molybdenum is the well-known spectrophotometric thiocyanate method[1]. However, this method has the disadvantage that when the molybdenum is reduced with tin(II) chloride in strong hydrochloric acid solution, maximum sensitivity is not obtained because of partial reduction to the molybdenum(III) state. Experiments in these laboratories have shown that, by attenuating the reducing power of the tin(II) chloride by keeping the hydrochloric acid concentration low, it is possible to obtain quantitative reduction of the molybdenum to the pentavalent state[2]. By extracting the molybdenum(V)-thiocyanate compound with methyl isobutyl ketone, high sensitivity in the molybdenum analysis is assured. The color of the ketone extract tends to fade rapidly but this difficulty can be eliminated by adding hydroquinone to the extract. This makes it possible to obtain good reproducibility in the analysis.

A serious disadvantage of maintaining a low hydrochloric acid concentration during the reduction of the molybdenum is that iron and vanadium interfere. Since the reduction of iron(III) is slow and incomplete, not much more than about 100 μg of this metal can be tolerated; not much more than about 50 μg of vanadium can be tolerated. However, the difficulty with iron and vanadium can be overcome by arranging to separate the molybdenum by solvent extraction with α-benzoinoxime-chloroform solution. As a result it has been possible to develop an excellent new method for the analysis of steel.

When reduction of molybdenum is made at low hydrochloric acid concentration, interference of tantalum, niobium and tungsten is negligible. This has made it possible to develop methods for the direct analysis of molybdenum in 0.1-g samples of these metals.

EXPERIMENTAL

Reagents

Standard molybdenum solution (10 μg per ml). Dissolve 0.252 g of $Na_2MoO_4 \cdot 2H_2O$ in water and dilute to 1 l. Dilute 100 ml of this solution to 1 l.

α-Benzoinoxime solution. Dissolve 2 g of α-benzoinoxime in 20 ml of ethanol by warming gently. Dilute to 200 ml with chloroform.

Tin(II) chloride solution. Dissolve 40 g of $SnCl_2 \cdot 2H_2O$ in 25 ml of hydrochloric acid (1 + 1) by heating, cool and then dilute to 100 ml. Prepare fresh every 2 or 3 days.

Ammonium thiocyanate solution. Dissolve 25 g of NH_4SCN in 500 ml of water in a polyethylene bottle.

Preparation of calibration graph

Transfer 0, 1.0, 2.0, 3.0 and 4.0 ml of standard molybdenum solution (10 μg per ml) to a 125-ml separatory funnel containing 10 ml of 10 % (w/v) citric acid solution plus 20 ml of sulfuric acid (1+4). Dilute to 70 ml, add 5 ml of tin(II) chloride solution and allow to stand for 5 min. Add 10 ml of ammonium thiocyanate solution. Add 10 ml of methyl isobutyl ketone and shake vigorously for 30 sec. Drain off and discard the lower layer plus about 0.25 ml of the ketone layer. Without delay, pour all but about 0.25 ml of the ketone extract into a dry 50-ml conical flask containing about 100 mg of hydroquinone. Swirl to dissolve the latter and then fill a 1-cm absorption cell. Allow to stand for 1 min to permit reduction of any molybdenum(VI) and then measure spectrophotometrically at 470 mμ using methyl isobutyl ketone as the reference liquid.

Analysis of steel

Dissolve a 25–500 mg sample containing up to 40 μg of molybdenum in 2–5 ml of freshly mixed hydrochloric acid–nitric acid (4+1) plus 2–15 drops of hydrofluoric acid, by warming gently in a covered 125-ml conical flask. Add 2 ml of perchloric acid (or 5 ml if the carbon content of the sample is over 1%) and evaporate until foaming ceases. Evaporate on a flame to a 0.5–1 ml volume. Cool, add 5 ml of hydrochloric acid and warm to dissolve salts and to reduce chromium(VI) and vanadium(V). Finally heat on a flame just to boiling to expel volatile oxidizing gases. Add 35 ml of water and cool.

Transfer the solution to a 125-ml pear-shaped separatory funnel and dilute to 50 ml. Add 10 ml of α-benzoinoxime solution and shake vigorously for 1 min. Drain off the lower layer into a 75-ml separatory funnel. If the two layers do not separate well because of the presence of carbides or colloidal acids of tungsten, niobium or tantalum, stir the interface with a stirring rod before removing the chloroform extract. Add 5 ml of chloroform to the aqueous solution, shake for 10 sec and drain off as before. If the separation of the layers has not been sharp, repeat the 5-ml chloroform wash. To the combined extracts add 15 ml of hydrochloric acid (5+95), shake for 10 sec and drain the chloroform extract into a dry 125-ml conical flask. Add 3 ml of chloroform to the aqueous solution, shake for 10 sec and drain off as before. If the separation of the layers has not been sharp repeat the 3-ml chloroform wash.

Evaporate the combined extracts on a low temperature hot plate until all chloroform has been expelled. Add 5 ml of sulfuric acid and heat to white fumes to carbonize the organic material. Cool, add 1 ml of nitric acid and 0.5 ml of perchloric acid (70%), cover and digest to destroy the readily oxidizable organic material. Raise the temperature to the point where the difficultly oxidizable organic material begins to be attacked by the perchloric acid. Hold at this temperature until the organic matter is completely oxidized. Finally, evaporate on a flame to 4 ml to expel all perchloric acid. Cool.

Add 20 ml of water and cool. Add 10 ml of 10% citric acid solution and transfer to a 125-ml separatory funnel, washing with 10 ml of water. Add 30 ml of water and proceed as directed in *Preparation of calibration graph.*

Analysis of tantalum or niobium metal

Direct analysis. Dissolve a 0.1-g sample of tantalum or niobium metal in a platinum crucible in 0.5 ml of hydrofluoric acid plus 3–5 drops of nitric acid by heating gently. Evaporate the tantalum sample on a sand bath to dryness or evaporate the niobium sample to moist dryness. Avoid baking the niobium sample, otherwise it may become difficultly soluble in hydrofluoric acid. Add 3 drops of hydrofluoric acid to the tantalum sample or 2 drops to the niobium sample and warm to dissolve the acid or oxide. Cool, add citric acid and sulfuric acid and proceed as directed in *Preparation of calibration graph.*

Analysis employing α-benzoinoxime separation. Dissolve the sample and obtain in solution in 3 drops of hydrofluoric acid. Add 5 ml of hydrochloric acid, dilute to 50 ml, add 10 ml of benzoinoxime solution and then proceed as directed in the *Analysis of steel.*

Analysis of tungsten metal

Direct analysis. Dissolve the sample and evaporate to dryness as directed in the method for tantalum or niobium. Add 2 ml of water and 1 pellet of sodium hydroxide and heat to dissolve the tungsten oxide. Ignore any insoluble hydroxides. Cool, add citric acid and sulfuric acid and proceed as directed in *Preparation of calibration graph.* If the ketone extract tends to be emulsified, filter it rapidly through a plug of glass wool into the 50-ml flask containing the hydroquinone. Correct for the interference of tungsten by dissolving 126 mg of pure WO_3 in 2 ml of water plus 1 pellet of sodium hydroxide and carrying the sample through the analysis.

Analysis employing a cupferron separation. After solution of the tungsten oxide in sodium hydroxide solution add 70 ml of water followed by 1 ml of hydrofluoric acid and then 5 ml of hydrochloric acid. Add 5 ml of freshly prepared aqueous 2% (w/v) cupferron solution, swirl and allow to stand for 30 sec. Extract for 30 sec with 10 ml of chloroform. Drain the lower layer plus a subsequent 3-ml chloroform wash to a 125-ml conical flask. Evaporate the combined extracts to expel chloroform and continue as directed in the α-benzoinoxime extraction and photometric determination of molybdenum in steel.

DISCUSSION

It seemed probable that the fading of the ketone extract in the spectrophotometric determination of molybdenum is due to air oxidation of molybdenum(V). Apparent confirmation of this was obtained when it was found that addition of sulfurous acid to the solution just before the addition of ammonium thiocyanate prevents the fading. However, the use of sulfurous acid had to be abandoned because it caused the extracts to be cloudy. This difficulty was eliminated by using hydroquinone as the reducing agent.

GOLDSTEIN *et al.*[3] have shown that, in the analysis of steel, molybdenum can be separated by an α-benzoinoxime–chloroform solvent extraction. Confirming this, tests in these laboratories have shown that quantitative separation from as much as 0.5 g of steel by a single solvent extraction with 1% α-benzoinoxime–chloroform solution is possible. The only metals that accompany the molybdenum in more than trace quantities in an α-benzoinoxime separation are chromium(VI), vanadium(V), niobium(V), tantalum(V) and tungsten(VI). In the proposed method for steel, chromium(VI) and vanadium(V) are reduced by boiling with hydrochloric acid, and the tantalum and niobium and more or less of the tungsten is precipitated by fuming with perchloric acid[4]. Most of the tungsten that escapes precipitation by the perchloric acid will accompany the molybdenum in the α-benzoinoxime separation[5].

At the low hydrochloric acid concentration used in the proposed method, the reduction of tungsten by tin(II) chloride is highly incomplete[5] and can be still further suppressed by the use of citric acid. The small amount of tungsten(V)-thiocyanate compound produced in the spectrophotometric determination of molybdenum will not interfere in the molybdenum analysis since the absorption of the tungsten compound at 470 mμ is negligible[5]. Typical results obtained in the analysis of NBS samples of steel are shown in Table I.

TABLE I

DETERMINATION OF MOLYBDENUM IN NBS STEEL SAMPLES

Sample	*Mo present (%)*	*Mo found (%)*
16c (C 1)	0.001	0.001, 0.001
125 (Si 5)	0.003	0.003, 0.003, 0.003
5j (C 2–Si 2)	0.005	0.005, 0.005
11g	0.005	0.004, 0.004, 0.004
170 (Ti 0.2)	0.006	0.006, 0.007, 0.006
121a (Cr 18–Ni 11)	0.020	0.017, 0.017, 0.017
155 (W 0.5)	0.039	0.039, 0.039, 0.039
19f	0.058	0.056, 0.057, 0.056
123a (Nb 0.75–Ta 0.02–W 0.11)	0.120	0.113, 0.114
121c (Cr 18–Ni 11–Ti 0.4)	0.160	0.160, 0.156

The interference of soluble tantalum and niobium in the proposed spectrophotometric thiocyanate method for molybdenum is negligible. It is true that the ketone extract from a 0.1-g sample of niobium metal is slightly yellow but the absorption of this yellow color at 470 mμ is equivalent to only about 0.5 μg of molybdenum. This makes it possible, on those samples containing less than about 100 μg of iron or 50 μg of vanadium, to make a direct analysis of molybdenum in 0.1-g samples of tantalum or niobium. Of course, if desired, it is possible to correct for the slight interference of niobium by dissolving 143 mg of pure niobic oxide in hydrofluoric acid and carrying it through the direct analysis as a blank. In the event that the sample to be analyzed contains appreciable amounts of iron or vanadium, it is best to resort to α-benzoinoxime separation to remove these interfering metals. In this separation some tantalum or niobium will accompany the molybdenum (and tungsten if present) but will cause no interference in the spectrophotometric determination of the molybdenum. Typical results obtained from the analysis of synthetic mixtures of pure Ta_2O_5 or Nb_2O_5 and sodium molybdate are shown in Table II.

What has been said above about the direct determination of molybdenum applies also to the analysis of tungsten metal except that the interference of the yellow color of tungsten in the ketone extract is greater than that of niobium. When analyzing a 0.1-g sample of tungsten metal, the absorption due to this metal is equivalent to about 2–3 μg of molybdenum. Thus, if a direct analysis of tungsten metal is to be made, it will be necessary to correct for the tungsten interference. When appreciable amounts of molybdenum are involved, the recoveries are somewhat low and emulsification of the ketone extract is more evident. These difficulties can be overcome by removing the tungsten with a cupferron separation[6]. In this case no correction for tungsten interference is needed. If the sample contains iron or vanadium, it may be necessary to follow the cupferron separation by an α-benzoinoxime separation. Typical results obtained from the analysis of synthetic mixtures of pure WO_3 and sodium molybdate are shown in Table II.

TABLE II

DETERMINATION OF MOLYBDENUM IN TANTALUM, NIOBIUM AND TUNGSTEN METAL

Mo added (μg)	*Tantalum*	*Niobium*	*Tungsten*
	Mo found (μg)	*Mo found (μg)*	*Mo found (μg)*
10	10.0[a]	10.0[a]	9.7[a]
10	10.0[b]	10.0[b]	10.2[b]
20	20.5[a]	20.0[a]	20.0[a]
20	20.0[b]	20.1[b]	20.0[b]
40	40.0[a]	39.5[a]	37.4[a]
40	40.2[b]	40.0[b]	39.0[b]

[a] Direct analysis.

[b] α-Benzoinoxime separation or cupferron separation used.

SUMMARY

A rapid, accurate spectrophotometric method for the determination of 0.001–0.1% of molybdenum in steel, tantalum, niobium or tungsten is presented. The molybdenum is isolated, when required, by solvent extraction with α-benzoinoxime–chloroform solution or cupferron–chloroform solution and then determined by the thiocyanate method. Conditions for obtaining high sensitivity by quantitative reduction of molybdenum(VI) to molybdenum(V) with tin(II) chloride have been established. It has been shown that fading of the molybdenum(V)–thiocyanate color can be minimized by adding hydroquinone to prevent air oxidation of molybdenum(V).

RÉSUMÉ

Une méthode rapide et précise est proposée pour le dosage spectrophotométrique du molybdène (0.001 à 0.1%) dans l'acier en présence de tantale, niobium ou tungstène. Le molybdène est séparé par extraction dans un solvant au moyen de solutions α-benzoïnoxime–chloroforme ou cupferron–chloroforme et dosé finalement par la méthode au thiocyanate. On a examiné les conditions de réduction du molybdène(VI) en molybdène(V) par le chlorure d'étain(II). Une addition d'hydroquinone permet d'éviter une oxydation du molybdène(V) à l'air.

ZUSAMMENFASSUNG

Es wird eine schnelle und genaue spektralphotometrische Methode zur

Bestimmung von 0.001–0.1% Molybdän in Stahl, Tantal, Niob oder Wolfram vorgeschlagen. Das Molybdän wird, falls erforderlich, durch Extraktion mit einer α-Benzoinoxim–Chloroform-Lösung oder einer Cupferron–Chloroform-Lösung extrahiert und anschliessend nach der Thiocyanatmethode bestimmt. Es werden die Bedingungen angegeben, die bei der quantitativen Reduktion des Molybdän(VI) zum Molybdän(V) mit Zinn(II)-Chlorid zu einer hohen Empfindlichkeit führen. Es konnte gezeigt werden, dass eine Farbänderung des Molybdän(V)-thiocyanats verringert werden kann, wenn Hydrochinon zur Verhinderung der Luftoxidation des Molybdän(V) zugegeben wird.

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SEPARATION OF LARGE AMOUNTS OF IRON(III) FROM COBALT, NICKEL, AND ALUMINIUM BY COMBINED ION EXCHANGE–SOLVENT EXTRACTION

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Previous investigations[1] have shown that large quantities of iron(III) can be separated from cobalt and nickel by means of anion exchange using Dowex 1 and a 90% acetone–10% 6 *M* hydrochloric acid mixture as eluant for the iron. As suggested previously, the non-adsorbability of iron from this medium is possibly due to the formation of a very stable ion-association complex between iron(III) chloride and the ketone which prevents adsorption of iron on the resin, although it is strongly retained on this resin from pure aqueous solutions containing a high percentage of acid, *e.g.* 6 *M* hydrochloric acid.

In order to see whether these separations could also be effected on a cation-exchange resin and if such a complex of iron is actually formed in organic solvent–hydrochloric acid media the present investigations were carried out using the strongly acidic cation-exchange resin Dowex 50. Tetrahydrofuran was selected as the solvent in order to demonstrate the close similarity of these ion-exchange processes with the conventional extraction method of iron(III) with ethers or ketones from 6 *M* hydrochloric acid solutions.

EXPERIMENTAL

Reagents and solutions

Ion-exchange resin. The strongly acidic cation-exchange resin Dowex 50-X8 (100–200 mesh, hydrogen form) was used for the batch and column experiments.

Standard solutions. Stock solutions of iron(III), cobalt, nickel, aluminium, and other elements were prepared by dissolution of the reagent-grade chlorides of these metal ions in 6 *M* hydrochloric acid.

Solvent. Tetrahydrofuran (THF) of reagent-grade purity.

Wash solutions. (*a*) 80% (v/v) THF + 20% 3 *M* hydrochloric acid; (*b*) 90% (v/v) THF + 10% 6 *M* hydrochloric acid.

Apparatus

Resin columns of 10 cm length and 1.0 cm in diameter were used.

Procedures

Determination of the elements. The same methods were used as earlier described in connection with the anion-exchange procedure[1].

Pretreatment of resin bed. The resin was soaked in a few milliliters of solution (*a*) and transferred to the ion-exchange column, and the resin bed was washed with 20–30 ml of this solution.

Sorption, washing and elution. Through the pretreated resin bed, 5–20 ml of a solution 80% in THF and 20% in 3 *M* hydrochloric acid containing iron and the elements to be separated was passed at a flow rate corresponding to the normal back-pressure of the column. During this operation iron(III) passed through unadsorbed while the other metal ions, *e.g.* cobalt, nickel, and aluminium, were strongly adsorbed on the top of the column. After passage of this solution the resin was washed with solution (*a*) to remove the last traces of iron(III); usually 40–50 ml were required. Then the resin was treated with solution (*b*) to elute the cobalt; under these conditions, nickel, aluminium, etc., were further strongly retained by the resin. The elution of cobalt was complete as soon as the deep blue color due to the cobalt–THF–hydrochloric acid complex was completely removed from the column; *ca.* 50 ml of solution (*b*) were usually needed. Finally nickel and/or aluminium were eluted with 50 ml of 6 *M* hydrochloric acid.

In the respective fractions, iron, cobalt, nickel, and aluminium were determined using titrimetric procedures[1].

RESULTS AND DISCUSSION

In Table I the batch distribution coefficients of iron, cobalt, nickel, and other metal ions which were measured in 80% and 90% tetrahydrofuran–hydrochloric acid media are recorded. In this Table the distribution values obtained in pure aqueous solutions of comparable acidity are included for the purpose of comparison.

From this adsorption data it can be seen that due to the small difference in the distribution coefficients of iron, cobalt, nickel, and aluminium in aqueous media no ready separation of these elements from each other is possible. Similar unfavorable conditions exist when the concentration of hydrochloric acid is varied, *i.e.* a separation of these metal ions is also difficult at higher or lower concentrations of hydrochloric[2] or other mineral acids such as nitric and sulfuric acid[3]. Particularly, the separation of cobalt from nickel is completely impossible in aqueous media containing hydrochloric, nitric, or sulfuric acid of any concentration; this is also true for perchloric acid media[4]. The distribution coefficients of cobalt and nickel are practically the same in aqueous–mineral acid media, but the adsorption of iron(III) at low acid concentrations is invariably higher than that of these elements; thus in the presence of large amounts of iron, large resin columns would have to be used to adsorb it quantitatively. Under these conditions aluminium is retained by the resin to about the same extent as iron so that a separation of these elements from each other is impossible. This behavior of the elements can be explained on the basis that the affinity of the cation-exchange resin for the divalent (Co and Ni) and the trivalent (Fe and Al) transition elements increases with an increase in the valency but is practically independent of the kind of element or mineral acid employed. This means that it is especially difficult to separate elements with like valency states by using pure aqueous mineral acid solutions.

If, however, at a constant concentration of hydrochloric acid the water is increasingly replaced by an organic solvent, *e.g.* tetrahydrofuran in the present case,

TABLE I

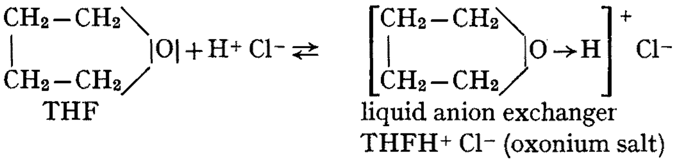
DISTRIBUTION COEFFICIENTS OF IRON, COBALT, NICKEL, AND OTHER METAL IONS IN TETRAHYDROFURAN–WATER MEDIA AT A CONSTANT ACIDITY OF 0.6 *M* HYDROCHLORIC ACID

(10% 6 *M* HCl; 1 g Dowex 50; 5 mg of metal ion as load)

Metal ion	*Percentage of tetrahydrofuran*		
	0%	80%	90%
Fe(III)	180	~1	~1
Co(II)	44.4	332	4.8
Ni(II)	46.7	411	107
Al(III)	242	>1,000	>1,000
Mg(II)	33	345	180
Ca(II)	77.5	>1,000	>1,000
Sr(II)	80	>1,000	>1,000
Ga(III)	235	~1	~1
In(III)	2	~1	~1
Pb(II)	34	6	~1
Bi(III)	~1	~1	~1
Cu(II)	32	3.5	~1
Zn(II)	38.8	~1	~1
Cd(II)	5	~1	~1
Ce(III)	>1,000	>1,000	>1,000
Gd(III)	>1,000	>1,000	>1,000
Ti(IV)	30	20	20
Zr(IV)	>1,000	>1,000	>1,000
Th(IV)	>1,000	>1,000	>1,000
V(IV–V)	5	4	3
Cr(III)	70	>100	>100
Mo(VI)	~2	~2	~2
UO$_2$(II)	28	11	~2
Mn(II)	53.3	153	26
Au(III)	~1	~1	~1

a marked difference in the adsorption values can be observed (see Table I). This difference is however much less, and can be practically non-existent, if nitric or sulfuric acid is used in place of the hydrochloric acid, or if water-miscible organic solvents other than ethers or ketones, *e.g.* aliphatic alcohols or liquid organic acids, are employed irrespective of the mineral acid simultaneously present. Consequently, this peculiar behavior of the elements, and especially of iron in tetrahydrofuran and also acetone[1], is dependent on the chemical constitution of the solvents (ether or ketone) and on the presence of hydrochloric acid. A similarity with the conventional method for the solvent extraction of iron and other metal ions from hydrochloric acid media by means of ethers and ketones is evident. (That this behavior is not directly connected with the dielectric constant of the organic component is evidenced by the fact that in this respect acetic acid should show the same effect as THF and *n*-propanol the same as acetone; but this is not the case.) It can therefore be assumed that the non-adsorbability of iron(III) from 80 or 90% THF–hydrochloric acid media (see Table I) is, like the liquid–liquid extraction of this element, due to a chemical reaction involving the formation of a complex which is so weakly dissociated that iron is not retained by the resin while the complexes of the other metal ions, *e.g.* cobalt, are more dissociated than that of iron and hence are exchanged for the hydrogen ion of the resin. Such a separation may therefore be referred to as a "combined ion exchange–solvent extraction" (CIESE) process[5] because both ion exchange and solvent extraction are operative simultaneously.

A ready explanation of this phenomenon can be offered by assuming that the THF or acetone forms with the hydrochloric acid present in the solution a liquid anion-exchange system (see eqn. (1)) which undergoes an anion-exchange reaction with the anionic iron(III) chloride complex (see eqn. (2)).



(1)

$$\mathrm{THFH^+Cl^- + (FeCl_4)^- \rightleftarrows THFH^+\,FeCl_4^- + Cl^-} \qquad (2)$$

liquid anion exchanger in
the iron(III) chloride form, *viz.*
ion association complex

Because at the same acidity iron is strongly adsorbed on the solid cation-exchange resin in absence of THF (see Table I), it is evident that the reactions shown by eqns. (1) and (2) are strongly dependent on the concentration of THF and on the acidity, *i.e.* with decreasing acidity at a constant concentration of THF the adsorption of iron on Dowex 50 also increases. That this behavior of iron, cobalt and several other elements (see Table I) seems to be an anion-exchange reaction in the liquid phase containing a high percentage of THF, is corroborated by the observation that when a solution containing iron and cobalt in a ratio of 1:1 or greater and containing 90% THF and 10% 6 *M* hydrochloric acid is passed through a column of the Dowex-50 resin, the cobalt is adsorbed on top of the resin bed whereas under the same conditions in absence of iron, it passes into the effluent much earlier. In other words in presence of iron the adsorption of cobalt is increased, *i.e.* its elution is retarded. This phenomenon ("elution retardation") can be explained by assuming that the liquid anion exchanger (see eqns. (1) and (2)) is heavily loaded with the anionic iron(III) chloride complex so that no exchange sites are available for the cobalt; thus the blue anionic chloride complex which is formed under these conditions of acidity and THF concentration, is continuously displaced from the liquid exchanger and is free to dissociate into its components so that cobalt is preferentially taken up as a cation by the solid cation-exchange resin. The same effect is observed when bismuth chloride, which is also known to form a strong anionic chloride complex, is used in place of iron chloride, although in this case the ratio of cobalt to bismuth must be very much higher[5].

All these observations can also be made by using acetone as the organic component. The non-adsorbability of iron(III) on a solid anion exchanger, *e.g.* Dowex 1 from a 90% acetone–10% 6 *M* hydrochloric acid medium[1], can similarly be explained by considering the reactions shown in eqns. (1) and (2). However, in this case there is a competition between a solid and a liquid anion exchanger, so that iron is less readily eluted than when Dowex 50 is used; the quaternary ammonium group of the solid anion exchanger is a stronger base than THF, and is more effective than the liquid exchanger in the competition for adsorbing the anionic chloride complexes from the liquid phase[5]. Several other phenomena encountered with CIESE processes, as well as with cation- or anion-exchange operations in general, can be explained by eqns. (1) and (2) or similar reactions[5].

The CIESE principle outlined in the working procedure on p. 309 was applied for the separation of large amounts of iron (500–1000 mg) from cobalt, nickel and aluminium and may also be utilized for its separation from various other metal ions which show high adsorbability under these conditions (see Table I). With this procedure the results obtained were similar to those shown in Table II of the previous paper[1]. However, much shorter columns and smaller volumes of eluant are required and no tailing of iron occurs, and this method therefore constitutes a considerable improvement over the anion-exchange method earlier reported[1]. The separations can be performed in a much shorter time, with the use of less reagent and with no sacrifice in accuracy or applicability. The method may also be applied to the determination of cobalt and nickel in the materials earlier mentioned[1]; it is superior to the conventional extraction techniques used for the removal of iron because immediately after elution of the iron, cobalt and nickel can be separated from each other (see *Procedure*), which is only possible by further manipulations in the case of a liquid–liquid extraction.

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SUMMARY

A method is described for the cation-exchange separation of large amounts of iron(III) from cobalt, nickel, and aluminium. On the strongly acidic Dowex 50-X8, iron(III) is not adsorbed from an 80% tetrahydrofuran–20% 3 *M* hydrochloric acid mixture, while cobalt, nickel, and aluminium are retained; a quantitative separation is thus possible. Cobalt and nickel or aluminium are then separated by elution with 90% tetrahydrofuran–10% 6 *M* hydrochloric acid. In these mixtures combined ion exchange–solvent extraction appears to occur; both ion exchange and liquid–liquid extraction are effective simultaneously.

RÉSUMÉ

Une méthode est décrite pour la séparation de grandes quantités de fer(III) d'avec le cobalt, le nickel et l'aluminium au moyen d'échangeur de cations. Le fer(III) en solution tétrahydrofurane (80%) et acide chlorhydrique 3 *M* (20%), n'est pas retenu sur résine Dowex 50-X8, contrairement au cobalt, au nickel et à l'aluminium. Ces derniers sont ensuite élués à l'aide du mélange tétrahydrofurane (90%)–acide chlorhydrique 6 *M* (10%). On réalise ainsi simultanément échange d'ions et extraction liquide–liquide.

ZUSAMMENFASSUNG

Es wird die Trennung grosser Mengen Eisen(III) von Kobalt, Nickel und Aluminium mit einem Kationenaustauscher beschrieben. Das Eisen(III) wird aus

einer Mischung von 80% Tetrahydrofuran und 20% 3 *M* Salzsäure vom stark sauren Dowex 50-X8 nicht adsorbiert, während Kobalt, Nickel und Aluminium zurückgehalten werden, so dass eine quantitative Trennung möglich ist. Kobalt und Nickel oder Aluminium werden dann durch Elution mit einer Lösung aus 90% Tetrahydrofuran und 10% 6 *M* Salzsäure getrennt. Es scheint eine Kombination aus Ionenaustausch und Lösungsmittelextraktion vorzuliegen.

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DETERMINATION OF ALUMINUM AND IRON BY SOLVENT EXTRACTION AND GAS CHROMATOGRAPHY

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Gas chromatography of metal fluoroacetylacetonates has become increasingly important in recent years. A recent book by MOSHIER AND SIEVERS[1] summarizes much of the work in this new field.

Recently several solvent extraction studies with trifluoroacetylacetone (TFA) have been reported[2-5]. In one of these studies, SCRIBNER *et al.* extracted aluminum and iron from aqueous acetate buffered solutions into chloroform using TFA[3].

The present study provides conditions for solvent extraction of aluminum and iron into benzene with TFA, and subsequent separation and determination by gas chromatography. In addition, a separation of iron from aluminum by solvent extraction and the determination of iron in the organic phase by spectrophotometry are reported.

EXPERIMENTAL

Apparatus

An F & M model 720 gas chromatograph equipped with a thermal conductivity detector containing tungsten filaments was used in this work. A piece of pyrex glass tubing was placed in the injection port of the chromatograph. Helium was the carrier gas and a 50-μl syringe with a Chaney adaptor was used for sample injection. A Carey model 14 recording spectrophotometer was used to obtain the visible spectrum of the iron chelate. A Beckman D.U. spectrophotometer was used for analytical measurements and a Perkin-Elmer Infracord was used to obtain infrared spectra. Solvent extractions were performed in A-8312 Duraglass bottles with 20–400 polyseal caps (Owen Illinois Glass Co.). A Burrel wrist action shaker was used to achieve equilibria in batch extractions. A Model G Beckman pH meter equipped with a 40495 glass electrode was used for equilibrium pH measurements. Initial pH measurements were taken with a 31983 Beckman combination electrode. Purity checks on iron-59 were made with an RIDL 200-channel pulse-height analyzer. Quantitative radioactivity measurements were made with an RIDL model 49–54 scaler.

Reagents

All reagents were of reagent grade unless otherwise specified. Iron-59 was obtained from Oak Ridge National Laboratory, Oak Ridge, Tennessee. Iron-59, as received, was contaminated with manganese-54 and cobalt-60. These impurities were separated from iron-59 by an anion-exchange procedure suggested by KRAUS AND NELSON[6]. Trifluoroacetylacetone was obtained from Columbia Organic Chemicals Co., Columbia, S.C. The reagent was distilled and the fraction boiling at 106–107° was collected.

Synthesis of chelates

Iron and aluminum trifluoroacetylacetonates were prepared so the spectra of each eluent could be compared to that of the pure chelate. Aluminum–TFA was prepared by a method described for the synthesis of tris(acetylacetonato) aluminum-(III)[7]. Iron–TFA was withdrawn from the benzene layer of several extraction flasks and the benzene was allowed to evaporate at room temperature. Both chelates were recrystallized from hexane and melting points which agreed with the literature values within 1° were obtained[8].

Chromatographic column

The column was made of 7.0 mm (o.d.) pyrex glass tubing 3.5 ft. long, and was bent into a helix. The column and solid support (glass micro beads, 60–80 mesh) were silanized with hexamethyldisilizane. The beads were coated 0.5% by weight with silicone DC-550 oil and the column was conditioned at 160°.

Solvent extraction studies

Initial solvent extraction studies were performed using $8 \cdot 10^{-3}$ M metal solutions. Iron solutions were made by dissolving iron wire in hot perchloric acid. A few drops of iron-59 were added to a liter of standard iron solution. The weight and volume of traces added were negligible. Aluminum solutions were made from aluminum nitrate.

25-ml volumes of aqueous solutions and 5-ml portions of organic phase were used. Radiometric measurements were made to follow the extraction of iron. The extraction curve for aluminum was obtained by measuring the amount of aluminum TFA in the organic phase by gas chromatography. A detailed description of each technique is given in an earlier publication[2].

Chromatographic calibration curves

The initial pH of each 25 ml aqueous phase containing aluminum was adjusted to a value between 7.5 and 9.5. This value was necessary since hydrogen ions are released upon chelation. The equilibrium pH was checked after injection of the sample to see that it was between 4.5 and 5.5. The pH of iron solutions was about 2.5 initially. Calibration curves were made by plotting the milligrams of metal initially in the aqueous phase *versus* the area of the chromatographic peak. The product of peak height and width at half the peak height was used for area measurements. Linear calibration curves were obtained for aluminum over the range of 1–4 mg/25 ml and 4–10 mg of iron per 25 ml.

Spectrophotometric working curve

Since the iron–TFA chelate is intensely colored, the spectrophotometric determination of iron in the benzene layer was also studied. The complex showed a broad maximum at 440 mμ. Using the same ratio of organic to aqueous phase as described above, a spectrophotometric working curve was obtained. The Beer–Lambert law was obeyed over the range of 0.2 to 4 p.p.m. of iron originally in the aqueous phase.

Chromatographic determination of iron and aluminum in synthetic mixtures

Known volumes of solutions containing 1–3 mg of aluminum and 4–8 mg of iron were pipetted into extraction flasks to give a total volume of 25 ml. Solutions were adjusted to a pH between 7.5 and 9.5 and 5-ml portions of 0.25 *M* TFA in benzene were added. The flasks were shaken for 4 h and 20-μl samples of organic layer were withdrawn and injected into the chromatograph which was maintained at 128°.

Determination of iron by spectrophotometry and aluminum by gas chromatography

Various volumes of standard aluminum and iron solutions were pipetted into extraction flasks to give a total volume of 25 ml. The aluminum was present in 2–4 mg amounts but only 0.4–2.4 p.p.m. of iron was present. The remainder of the procedure was identical to that described above with the exception that a 3.0-ml portion of the organic phase was placed in a 1-cm cell and the iron was determined spectrophotometrically.

Separation of iron from aluminum by solvent extraction

Extraction flasks again contained 25 ml of solution. Aluminum was in the same concentration as described previously and iron was present in either milligram or microgram quantities. The pH was adjusted to a value between 1.5 and 2.0 and iron was determined by either gas chromatography or spectrophotometry. Each extract was checked for aluminum by gas chromatography but none was found.

Interference study

The effect of diverse ions on the method was studied by adding known quantities of various salts to solutions containing 2 mg of aluminum and 6 mg of iron. Iron and aluminum were determined by gas chromatography as described previously. The molar concentration of each ion added was originally 100 times that of the iron. If significant interference occurred, the concentration of the interfering ion was decreased until the error was reduced to a value less than 5%. All metal ions were added as nitrates and diverse anions were added as either sodium or potassium salts.

In order to reduce the interference resulting when copper or nickel was present, picolinic acid was added. To extraction flasks containing 2 mg of aluminum, 6 mg of iron and either 170 mg of copper or 157 mg of nickel, 1.10 g of picolinic acid was added.

Analysis of a nickel–copper alloy

A 1.400-g sample of National Bureau of Standards alloy, 162A, was placed in a 100-ml beaker and dissolved in 10 ml of hot concentrated perchloric acid. After dissolution of the sample, about 25 ml of distilled water was added. The solution was then filtered through Whatman Blue-line filter paper to remove the silica. The precipitate was washed thoroughly with distilled water and the filtrate and washings were diluted to the mark in 100-ml volumetric flasks.

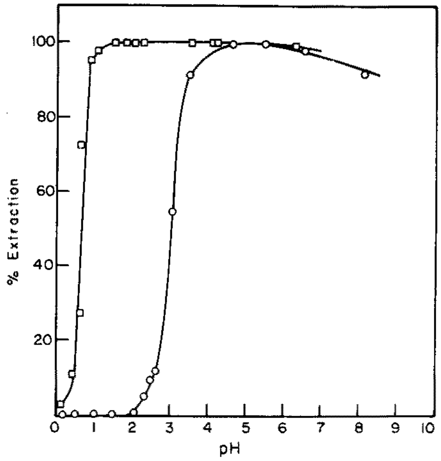
Twenty-five-ml aliquots of each solution were transferred to extraction flasks. A 3.5 mole ratio of picolinic acid per mole of copper and nickel was added to each flask. The pH was brought to about 5.5 with 6 *M* and 1 *M* sodium hydroxide. The remainder of the procedure was the same as that used for the synthetic mixtures.

RESULTS AND DISCUSSION

The extraction curves for aluminum and iron are shown in Fig. 1. The equilibrium pH is given on the diagram and is lower than the initial pH since hydrogen ions are released during extraction. These results for the extraction of iron and aluminum with TFA into benzene agree closely with those obtained by SCRIBNER[3] for extractions into chloroform. It is evident from Fig. 1 that a separation of iron from aluminum is possible at low pH. This separation was performed with both milligram and microgram quantities of iron and the results are shown in Tables I and II. Since iron interferes in many aluminum determinations this separation should be quite useful.

A spectrophotometric method was developed using the intense red color of the iron chelate. The spectrum shows peaks at 440 mμ and 375 mμ. Using the 440-mμ peak, the molar absorptivity of the chelate in the organic phase was found to be 3,860/mole/cm. This method was used to determine iron which was extracted with aluminum and also for iron which was separated from aluminum. The results of the former are given in Table III and those for the separation are listed in Table II. The average relative error for both series combined was 1.85%.

The gas chromatogram for the separation of aluminum and iron chelates is shown in Fig. 2. No evidence of decomposition of either chelate was found in the glass injection port after a series of samples had been analyzed. Moreover, the infrared



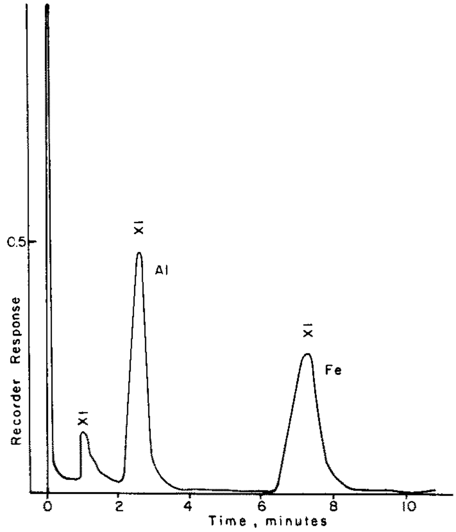


Fig. 1. Effect of pH on the extraction of Al(III) and Fe(III) by 0.25 *M* TFA in benzene. □, $8 \cdot 10^{-3}$ *M* Fe; ○, $8 \cdot 10^{-3}$ *M* Al.

Fig. 2. Separation of Al(TFA)$_3$ and Fe(TFA)$_3$ by gas chromatography. Column temperature 128°, flow rate 80 ml/min, injection port temperature 135°, detector temperature 150°.

spectrum of the eluent for each metal was identical to that of the pure chelate.

The results for a series of synthetic unknowns which were analyzed by solvent extraction and gas chromatography are given in Table IV. The mean relative error was 2.86% for aluminum and 1.60% for iron.

TABLE I

SEPARATION OF IRON FROM ALUMINUM

(Iron determined by gas chromatography)

Sample	*Iron*				*Aluminum*	
	Present (mg)	*Found (mg)*	*Absolute error (mg)*	*Relative error (%)*	*Present (mg)*	*Found (mg)*
1	6.00	5.98	0.02	0.33	2.00	0.00
2	6.00	6.10	0.10	1.67	3.00	0.00
3	4.00	4.16	0.16	4.00	4.00	0.00
4	8.00	8.10	0.10	1.25	2.00	0.00
5	4.00	4.16	0.16	4.00	3.00	0.00

TABLE II

SEPARATION OF IRON FROM ALUMINUM

(Iron determined by spectrophotometry)

Sample	*Iron*				*Aluminum*	
	Present (p.p.m.)	*Found (p.p.m.)*	*Absolute error (p.p.m.)*	*Relative error (%)*	*Present (mg)*	*Found (mg)*
1	2.40	2.44	0.04	1.66	2.00	0.00
2	1.60	1.58	0.02	1.25	3.00	0.00
3	0.80	0.82	0.02	2.50	3.00	0.00
4	2.40	2.43	0.03	1.25	2.00	0.00
5	0.40	0.39	0.01	2.50	4.00	0.00

TABLE III

DETERMINATION OF ALUMINUM BY GAS CHROMATOGRAPHY AND IRON BY SPECTROPHOTOMETRY

Sample	*Aluminum*				*Iron*			
	Present (mg)	*Found (mg)*	*Absolute error (mg)*	*Relative error (%)*	*Present (p.p.m.)*	*Found (p.p.m.)*	*Absolute error (p.p.m.)*	*Relative error (%)*
1	2.00	1.95	0.05	2.50	2.40	2.43	0.03	1.25
2	3.00	3.04	0.04	1.33	1.60	1.62	0.02	1.24
3	4.00	3.85	0.15	3.95	1.60	1.61	0.01	0.62
4	2.00	1.93	0.07	3.50	1.00	0.97	0.03	3.00
5	3.00	2.98	0.02	0.67	0.40	0.39	0.01	2.50
6	4.00	3.90	0.10	2.50	0.80	0.82	0.02	2.50

Table V shows the effect of various ions on the method. Most metals present in high concentration were found to interfere. Most interferences resulted from emulsion formation. When this emulsion became quite noticeable, the organic phase was not sampled with a syringe for fear of plugging up the syringe or contaminating the

TABLE IV

DETERMINATION OF ALUMINUM AND IRON BY GAS CHROMATOGRAPHY

	Aluminum				*Iron*			
Sample	*Present (mg)*	*Found (mg)*	*Absolute error (mg)*	*Relative error (%)*	*Present (mg)*	*Found (mg)*	*Absolute error (mg)*	*Relative error (%)*
1	2.00	1.90	0.10	5.00	6.00	5.95	0.05	0.83
2	1.00	1.02	0.02	2.00	8.00	8.20	0.20	2.50
3	2.00	1.97	0.03	1.50	6.00	6.10	0.10	1.67
4	1.00	1.02	0.02	2.00	8.00	8.20	0.20	2.50
5	3.00	2.90	0.10	3.33	4.00	4.05	0.05	1.25
6	3.00	2.90	0.10	3.33	4.00	4.03	0.03	0.75

chromatographic column. When large amounts of nickel were present, iron and aluminum were not completely extracted. Since some precipitate formed when nickel was present, the infrared spectrum of the precipitate was obtained. The spectrum showed similarities to that of nickel hydroxide and the TFA chelate. Copper was extracted with the other two species and was not resolved from the iron peak using the chromatographic conditions listed. Both copper and nickel interferences were

TABLE V

EFFECT OF DIVERSE IONS

(2.00 mg of aluminum and 6.00 mg of iron added)

Species	*Added (mg)*	*Molar ratio diverse ion/Fe*	*Al relative error (%)*	*Fe relative error (%)*
Cl^-	381	100	2.67	3.05
NO_3^-	666	100	2.00	2.50
SO_4^{2-}	1052	100	4.10	3.13
$C_2O_2H_3^-$	644	100	4.33	3.20
Ni^{2+}	630	100	[a]	
	157	25	5.00	4.00
	157	25[b]	0.00	1.00
Cu^{2+}	682	100	[a]	
	170	25	21.40	[c]
	170	25[b]	1.25	2.60
Co^{2+}	633	100	[a]	
	158	25	3.50	12.50
	63	10	1.50	4.40
Cr^{3+}	558	100	[a]	
	140	25	[a]	
	56	10	2.50	4.50
Mn^{2+}	590	100	[a]	
	147	25	[a]	
	59	10	2.50	6.80
	5.9	1	2.10	3.60
Zn^{2+}	702	100	[a]	
	175	25	2.50	1.70

[a] Intense emulsion formation, no injection made.
[b] Picolinic acid added.
[c] Iron and copper peaks unresolved.

overcome by masking these ions with picolinic acid. Both the copper and nickel picolinates are rather stable in this pH range; the logarithms of the conditional stability constants at pH 5.0 are 12.0 and 12.7 for copper and nickel respectively[9]. Furthermore, picolinic acid is an effective buffer in this region ($pK_a = 5.23$)[10].

Iron and aluminum were determined in a nickel–copper alloy, NBS-162A, which contained 64.00% nickel, 30.60% copper and minor amounts of other elements. The results of the analysis of this alloy are given in Table VI. Very good agreement with the average value listed by the National Bureau of Standards was obtained. Again picolinic acid served as both a buffer for the pH region needed, and as an effective masking agent for copper and nickel.

TABLE VI

ANALYSIS OF NATIONAL BUREAU OF STANDARDS ALLOY 162A

Sample	*Weight of Al found (mg)*	*Al found (%)*	*N.B.S. value (%)*	*Weight of Fe found (mg)*	*Fe found (%)*	*N.B.S. value (%)*
1 A	1.75	0.500	0.50	7.40	2.12	2.19
2 A	1.70	0.485		7.60	2.17	
3 A	1.71	0.488		7.41	2.12	
4 A	1.75	0.500		7.59	2.17	
1 B	1.78	0.508		7.85	2.24	
2 B	1.79	0.511		7.85	2.24	
3 B	1.79	0.511		7.87	2.25	
4 B	1.78	0.508		7.87	2.25	

SUMMARY

A method which combines solvent extraction and gas chromatography for the determination of aluminum and iron in the same sample is given. The two metals were extracted into benzene with trifluoroacetylacetone and a portion of the benzene layer was injected into a gas chromatograph. The two chelates gave well resolved symmetrical peaks. The method was tested by analyzing a National Bureau of Standards alloy, number 162A. Copper and nickel, which would normally interfere when present in large amounts, were masked with picolinic acid. In addition a solvent extraction separation of iron from aluminum and a spectrophotometric determination of iron is described.

RÉSUMÉ

Une méthode est proposée pour le dosage de l'aluminium et du fer dans un même échantillon, combinant extraction dans un solvant et chromatographie gazeuse. Les deux métaux sont extraits dans le benzène au moyen de trifluoracétylacétone; une portion de la couche benzénique est injectée dans le chromatographe. Ce procédé a été expérimenté pour l'alliage No 162 A du "National Bureau of Standards". Le cuivre et le nickel peuvent être masqués par l'acide picolinique. On décrit également une séparation du fer d'avec l'aluminium et un dosage spectrophotométrique du fer.

ZUSAMMENFASSUNG

Es wird eine Methode zur Bestimmung von Aluminium und Eisen in der gleichen Probe beschrieben, bei der die Flüssigextraktion mit der Gaschromatographie kombiniert wird. Die Metalle werden unter Zugabe von Trifluoroacetylaceton mit Benzol extrahiert und ein Teil des Benzols in einen Gaschromatographen gegeben. Die 2 Chelate ergeben gut aufgelöste symmetrische Maxima. Kupfer und Nickel, die normalerweise, wenn sie in grossen Mengen anwesend sind, stören, werden mit Pikolinsäure maskiert. Zusätzlich wird die Trennung des Eisens vom Aluminium mit der Flüssigextraktion und spektralphotometrischer Bestimmung beschrieben.

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IDENTIFICATION AND DETERMINATION OF PHENOLS AND CHLOROPHENOLS IN VERY DILUTE AQUEOUS SOLUTIONS BY GAS-LIQUID CHROMATOGRAPHY, PAPER CHROMATOGRAPHY AND SPECTROPHOTOMETRY

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In the international standards for drinking water[1] the following values are given for phenolic substances: maximum acceptable concentration 0.001 mg per litre, and maximum allowable concentration 0.002 mg per litre, both measured as phenol. The phenolic compounds are determined by the 4-aminoantipyrine method. However, most *p*-substituted phenols are not determined by this method and there is some confusion about it in the literature; some say that *p*-substituted phenols as a whole are not determined[2], whereas others exclude only phenols with certain groups such as methyl in the *p*-position[3]. Moreover, the response of 4-aminoantipyrine to other substituted phenols is less than the response to phenol itself[4,5].

In surface water phenols may be present from natural sources[6], from biological decay of certain pesticides[2] and from industrial waste. The last group includes phenol, cresols, xylenols and their chlorination products. The chlorination of phenol yields mainly 2- and 4-chlorophenol, 2,4- and 2,6-dichlorophenol and 2,4,6-trichlorophenol[7]; on stronger oxidation ring rupture occurs[8]. Some of these chlorination products, the 2-chloro- and the dichlorophenols, possess a strong odour even at high dilutions but with the others the threshold odour concentration is larger[9,10]. It is thus possible that the phenol content of surface waters after receiving chlorinated waste, or even of drinking water after treatment with chlorine, is only partially measured by the aminoantipyrine method while the odour of the water after a strong or mild chlorination cannot be predicted at all. Chlorophenols are less decomposed by microbiological action and probably biological attack is more difficult, the larger the chlorine content; trichlorophenol can be expected even after a long period in a storage reservoir or in the soil, whereas the unchlorinated phenol will have disappeared.

According to MOHLER AND JACOB[5] the 4-aminoantipyrine method is the best of the spectrophotometric procedures and the ultraviolet method the most promising. The diazotization of phenols[11,12], which was not considered by MOHLER AND JACOB, proceeds on the *p*-position, but is also possible on the *o*-position, when the *p*-position is blocked. This method has also serious drawbacks; the colour is not stable, the response of different phenolic compounds varies largely and the colour varies with concentration. Ultraviolet spectrophotometry can be made specific for phenols by using the difference spectrum of the phenol and the phenolate. There is a bathochromic shift of the maximum to longer wavelengths in alkaline solutions[8,13-15]. However, the sensitivity is lower than with the 4-aminoantipyrine method, so that the ultraviolet method can generally be used only after a previous concentration procedure. The methods mentioned give the total phenols and the possibility of recognizing groups of phenols is very small.

Infrared spectrophotometry furnishes good identification of pure compounds but with mixtures it usually indicates only the presence of various groups. Paper chromatography offers the possibility of identifying phenols individually, but certain isomers and homologues cannot be differentiated (*e.g.* cresols) and only semiquantitative estimations are possible.

Gas–liquid chromatography is the most promising method, in spite of some contradictory experiences found in literature[6,16,17]. However, it is necessary to separate the group of phenols first and to choose a good stationary phase capable of resolving compounds with similar boiling points.

To obtain more information about the individual phenols, concentration and separation from other groups of organic substances is necessary. SCHOLZ[18] concentrated the phenols in alkaline solution by evaporation of the water and volatile organic substances in vacuum. The phenolates together with inorganic salts and salts of organic acids remain in the residue. MIDDLETON *et al.* introduced the carbon–chloroform extraction method[19], which is now a standard method for water in the U.S.A.[20]. The weight of the residue after evaporation of the chloroform is a measure of the pollution of the water with noxious organic substances. The influence of probably harmless organic substances such as humic acids occurring in smaller or larger quantity in natural water is small. Other concentration techniques, such as extraction, freezing-out, use of other adsorbents, ion exchange, have hitherto given difficulties when adapted for the isolation of organic substances from large quantities of water.

To obtain more information about the individual phenols present in water from different sources, the following working scheme was chosen:

(*1*) Isolation of the organic substances by a standard or modified carbon–chloroform extraction method.

(*2*) Separation of the phenols as in the scheme of SHRINER *et al.*[21].

(*3*) Identification of the individual phenols by gas chromatography.

(*4*) Confirmation of the gas-chromatographic results by paper chromatography, ultraviolet differential spectrophotometry and infrared spectrophotometry.

(*5*) Estimation of the quantities of individual phenols with the aid of gas chromatography.

Isolation of the organic substances by the carbon–chloroform extraction method

The mechanism of adsorption on active carbon is two-fold: a rapid adsorption at the surface of the particles and a slower diffusion into the pores of the particles[22]. During the exposure time the carbon does not reach saturation and the adsorption is complete even with a short contact time in the column, when the current of water encounters surfaces again capable of adsorption after the initially adsorbed matter has migrated into the pores. When adsorption is continued for a long time, growth of algae and bacteria can cause difficulties and the possibility of interferences. To decrease the growth of these organisms silver grains previously etched with nitric acid were placed in the column. (After use, the silver surfaces were cleaned in a bath of 2 *M* sodium hydroxide and aluminium turnings.) It is generally accepted that the adsorption of the phenolic substances on active carbon is fairly complete but it has often been found that desorption is only about 80% complete. In the course of another investigation it was found that desorption of phenol was 82–98% complete using a batch procedure with methanol. In the standard procedure the extraction time in the Soxhlet apparatus is 35 h. Other important factors are the size of the carbon particles, the wetting by the chloroform, the number of extractions and the amount of carbon compared to the capacity of the extractor. When the size of the carbon particles is not too small, clotting of the particles is prevented and wetting by chloroform is more effective. On the other hand, it is more difficult to remove water from the coarser particles. The drying must be prolonged after the carbon is free-flowing and appears like fresh unused carbon, otherwise a water layer is formed during extraction; but prolonged drying causes a larger loss of volatile substances. To avoid these difficulties in the present experiments the free-flowing carbon was extracted once with some methanol in a batch procedure. The remaining water and a small quantity of the organic substances were dissolved in the methanol in this way and the residue after evaporation of the alcohol was added to the main portion.

The number of extractions may vary between 25 and 50. When the upper part of the extraction column is only partly filled with carbon, conditions can be chosen so that the whole column is immersed in the chloroform for 15 min in each cycle of the extraction. With these precautions desorption and recovery can be expected to reach an acceptable value.

Residues were received from a waterwork where the standard procedure was slightly modified and active carbon samples were obtained from batch procedures using carbon powder*.

Separation into groups

The residue obtained by evaporation of the chloroform was redissolved as far as possible in ether and separated as described by Shriner *et al.*[21] by extraction with

TABLE I

SEPARATION INTO GROUPS

Sample	*Total residue ($\mu g/l$)*	*Soluble in ether ($\mu g/l$)*	*Residue soluble in ether (%)*					
			Acidic	*Phenolic*	*Neutral*	*Basic*	*Amphoteric*	*Loss*
2[a]	640	428	30	8	29	10	6	17
3[b]	206	161	33	8	25	9	6	19
4[c]	40	30	19	8	34	4	3	31
5[c]	56	47	11	6	32	4	2	46
6[c]	32	23	15	7	52	1	1	24
7[c]	34	25	8	6	49	4	3	30

[a] Raw surface water after filtration and chlorination.
[b] Drinking water prepared from 2 by infiltration and ordinary treatment.
[c] Treated surface water from another plant collected at different times.

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* We thank Mr. A. P. Meyers (Lab. Chem. Technology, Delft), who is working at the development of new techniques for the concentration of organic substances from water, for setting at our disposition a number of these carbon samples.

aqueous solutions at different pH values. The content of each of the 5 groups—acids, very weak acids (predominantly phenols), neutral, basic and amphoteric substances—was found by evaporation (Table I).

During the separation procedure, losses were caused by evaporation and by incomplete separation. The losses by evaporation occurred mainly during the difficult removal of the last drops of liquid from the residue. This liquid was not chloroform or ether but some water dissolved in the organic liquid during the extraction. To decrease the losses the evaporations could be carried out in vacuum at 30°, but theoretical losses amount to 48% with phenol and to 3% with trichlorophenol after 3 evaporations. The theoretical losses were calculated from the equation[23]

$$\log(100-c) = 2 - \frac{P_B}{P_A} \log \frac{A_1}{A_2}$$

where c is the loss of phenol (%), P_A the vapour pressure of the solvent, P_B the vapour pressure of the phenol, A_1 the amount of solvent at the start of the evaporation, and A_2 the amount of solvent at the end of the evaporation.

When 100 ml of ether containing 1 ml of water were evaporated to a volume of 1 μl, the main losses occurred during the evaporation of the water after the ether had disappeared. The losses calculated in this way agreed within 10% absolute with the losses found in practice. Thus, in carrying out the separation procedure, a choice must be made. The weights of the different fractions can be determined, but the losses are considerable and only the less volatile substances are found, which gives only a rough impression of the total content of organic substances. Alternatively, emphasis is laid on the determination of individual compounds after separation into groups. The last drops of liquid are not evaporated, and more volatile compounds are found, but the total weights of the different groups remain unknown. It is possible to dry the ether after the extractions with magnesium sulphate or with molecular sieve but then the whole extraction procedure takes a long time and some adsorption of the organic substances by the drying agent is very probable.

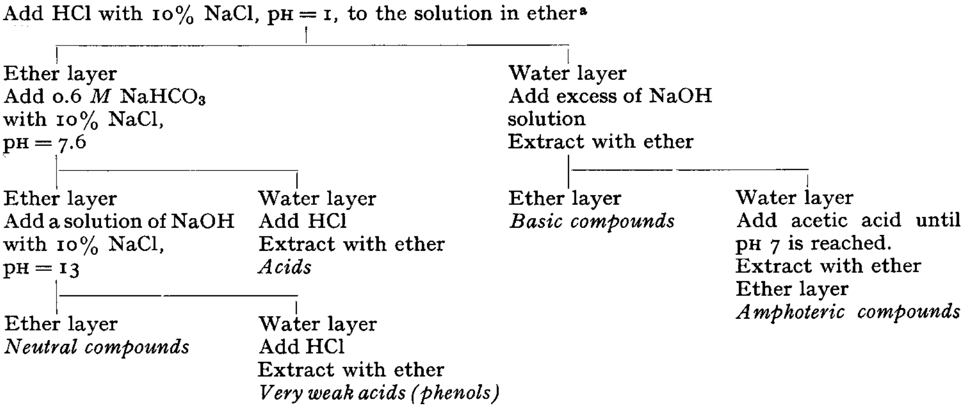
The separation itself is imperfect and it is important to obtain further knowledge about it. In our first experiments, the separation was tested on a tar found on the bank of the river Rhine (Lek at Schoonhoven). This tar was more easily accessible in large quantities than the residues obtained by carbon–chloroform extraction. The content of neutral compounds was much higher (93% of the ether-soluble fraction) than with residues from water—which was expected—but all fractions were present. Similar results were obtained in an investigation of oil tar materials from Southern California beaches[24]. The chloroform extract of the tar from Schoonhoven was separated into 2 portions and a standard solution containing 12 phenols in benzene was added to one of the portions. The 12 phenols were all found in the phenolic group by gas chromatography but recovery was far from quantitative owing to losses by evaporation on the water bath. In the phenolic group of the other portion no phenols could be identified.

More quantitative results were obtained by adding 6 phenols to a residue which itself contained smaller quantities of these 6 phenols (phenol, 2-cresol, 3-cresol, 2,4-xylenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol). The recoveries after 3 evaporations in vacuum varied from 58% with phenol to 90% with trichlorophenol in accordance with theory. The recovery of 2,4-xylenol was very low, 54% instead of about 85% theoretically. However, the 2,4-xylenol was also found in the neutral group, when the same gas-chromatographic procedure was applied to that group. The acidic dissociation constant of 2,4-xylenol (pK_a = 10.45 at 25°) is in the same range as the dissociation constants of other methyl-substituted phenols. It is therefore difficult to explain the deviating behaviour of the 2,4-xylenol.

Several separation schemes, adapted from the original scheme of SHRINER *et al.*, are given in the literature[19,24-26]. In some of these schemes the ether solution is extracted with water. The water is unbuffered and its pH depends on the organic substances extracted. This extraction with water can give an uncontrollable loss of organic substances and is better omitted.

TABLE II

SEPARATION OF ORGANIC SUBSTANCES



Add HCl with 10% NaCl, pH = 1, to the solution in ether[a]

Ether layer
Add 0.6 *M* $NaHCO_3$
with 10% NaCl,
pH = 7.6

Ether layer
Add a solution of NaOH
with 10% NaCl,
pH = 13

Ether layer
Neutral compounds

Water layer
Add HCl
Extract with ether
Very weak acids (phenols)

Water layer
Add HCl
Extract with ether
Acids

Water layer
Add excess of NaOH
solution
Extract with ether

Ether layer
Basic compounds

Water layer
Add acetic acid until
pH 7 is reached.
Extract with ether
Ether layer
Amphoteric compounds

[a] Three extractions were made in each case.

TABLE III

RECOVERIES AFTER SEPARATION

Component	*Recovery (%)*	*Component*	*Recovery (%)*
Phenol	90	2-Nitrophenol	82
4-Cresol	93	2-Cresol	90
2,4-Xylenol	54	3-Cresol	95
4-Ethylphenol	80	2,5-Xylenol	78
2,4,6-Trichlorophenol	92	2,4-Dichlorophenol	87
Guaiacol	—[a]	4-Chlorophenol	95

[a] Quantitative estimation from the chromatogram not possible.

The pH of the aqueous solutions used in the extraction procedure is very important. To control the effectiveness of the separation scheme 2 mixtures containing each 6 phenols and *p*-quinone were treated by the scheme shown in Table II. The pH values of the aqueous solutions were measured. The most important extraction, that with a solution of sodium hydrogen carbonate, occurred at pH 7.6. Most of the phenols gave recoveries in the range 87–95%; 2-nitrophenol being a slightly stronger acid (pK_a = 7.21) gave a recovery of 82%, and 4-ethylphenol and 2,5-xylenol of 80 and

78% respectively but 2,4-xylenol showed again a very low 54% (Table III). The *p*-quinone was not found in the phenolic group. Sodium chloride was added to the extracting media to diminish emulsification. The first samples were treated as in the scheme of Shriner *et al.*; the scheme finally adopted for quantitative work is outlined in Table II.

Identification of the individual phenols by gas chromatography

Methods of separation and characterisation of phenols by gas–liquid chromatography have been proposed by Karr *et al.*[27], Brooks[28], Fitzgerald[29], Kolšek and Maticic[30], Kollof *et al.*[31], Scholz[18] and others. With common stationary phases such as Apiezon-L, separation between 3- and 4-cresol is impossible and separation of other components is poor. In the present work, tris(2,4-xylenyl) phosphate was chosen as stationary phase; this gives an excellent separation of phenols, cresols and

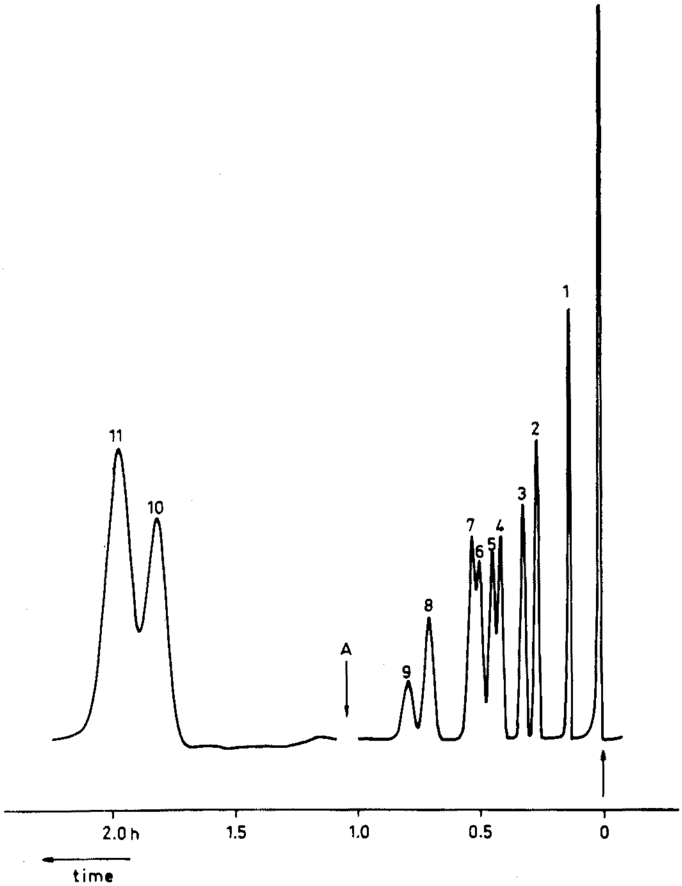


Fig. 1. Gas chromatogram of a standard mixture of phenols. Injection $5\ \mu l$ containing $20.8\ \mu g$ of each phenol. At A, the sensitivity was increased ten-fold. (1) guaiacol, (2) phenol, (3) 2-cresol, (4) 4-cresol, (5) 3-cresol, (6) 2,4-xylenol, (7) 2,5-xylenol, (8) 4-ethylphenol, (9) 2,4-dichlorophenol, (10) 2,4,6-trichlorophenol, (11) 4-chlorophenol.

xylenols, but has not previously been applied to mixtures containing chlorophenols. The tris(2,4-xylenyl) phosphate was prepared from 2,4-xylenol and phosphoryl trichloride as described by KREYSLER[32]. The product was distilled at a pressure of 0.4 mm mercury and the fraction from 210 to 215° was collected. The advantage over similar commercial products, that are often mixtures of isomers, is a better defined product which results in a better separation.

The choice of the phenols used for the standard mixture was made according to the following considerations. Phenol and the 3 cresols are the main products in the raw phenol fraction of tars, and 2,4- and 2,5-xylenol are the most important representatives of the xylenols in this fraction. Guaiacol, 2-nitrophenol, 4-ethylphenol are among the most common substances in other classes of phenolic compounds, whereas 4-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol are important chlorination products of phenol.

The gas chromatograph used was composed of a thermostat (Becker Delft type 1452 SH) and a flame detector (Becker Delft type 2032 EJL). The column with a length of 1.5 m and an inner diameter of 4 mm was filled with Chromosorb W 60/80 containing 5% xylenyl phosphate. The carrier gas was hydrogen at a pressure of 1 kg/cm^2 and a flow of 80 ml/min. The temperature of the thermostat was 130° and air with an inlet pressure of 0.65 kg/cm^2 was used for the flame.

The shape of the curve and the retention times found with a standard mixture of phenols in benzene (concentration of each phenol about 4 mg/ml) are given in Fig. 1 and Table IV respectively. After the column had been used for a month, the retention times were reduced to 90% of the original values. It was therefore necessary to control the retention times of the standard mixture from time to time.

TABLE IV

RETENTION TIMES WITH XYLENYL PHOSPHATE ON CHROMOSORB W

	Component	*Retention time (min)*		*Component*	*Retention time (min)*
1	Guaiacol	8.2	7	2,5-Xylenol	31.9
2	Phenol	15.9	8	4-Ethylphenol	42.3
3	2-Cresol	19.2	9	2,4-Dichlorophenol	47.4
4	4-Cresol	24.8	10	2,4,6-Trichlorophenol	109.3
5	3-Cresol	26.8	11	4-Chlorophenol	118.5
6	2,4-Xylenol	29.9			
				2-Nitrophenol	10.3

The residues obtained in the phenolic group of the different samples were dissolved in 1–2 ml of benzene and chromatographed. With all samples distinct peaks were obtained (Figs. 2, 3 and 4). Sometimes it was necessary to change the concentration of the solution, the amount injected or the sensitivity to obtain a good chromatogram. All peaks could be identified except 3 peaks of sample 5, and 5 peaks of sample 7. It is thought that some of these unknown peaks could be attributed to chlorocresols. From the 3 cresols 12 isomers can be derived theoretically by chlorination in aqueous medium. Further work is being done in this direction.

In sample 3 a very small peak was found with the same retention time as *p*-quinone. Confirmation by other methods was impossible owing to the extremely small concentration; when *p*-quinone was actually present it was an artefact formed by oxidation after the separation scheme had been carried out.

Table V shows the phenols which were found in the different samples.

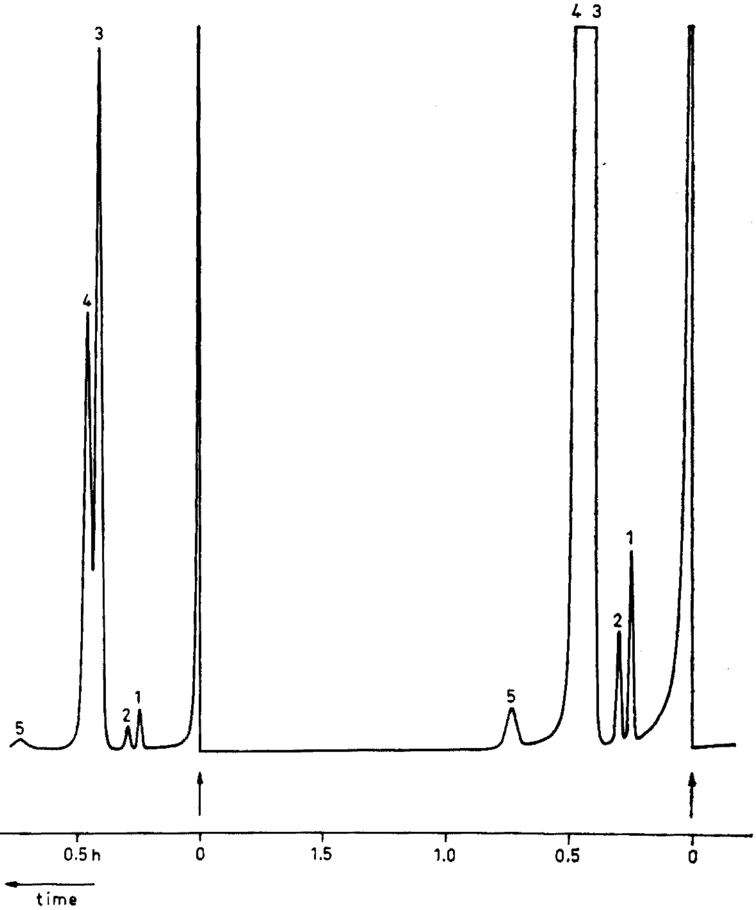


Fig. 2. Gas chromatogram of the phenols in sample 1. First injection 10 µl, second injection 1 µl. (1) phenol, (2) 2-cresol, (3) 3-cresol, (4) 2,4-xylenol, (5) 2,4-dichlorophenol.

Paper chromatography

For the separation of phenols the method proposed by RILEY[33] and LEDERER AND LEDERER[34] was used. This method is based on the use of a mixture of butanol and benzene saturated with water as the mobile phase and molybdophosphoric acid as the spraying agent. The spots were fixed by exposure to ammonia vapours. The whole analysis required about 7 h and the minimum detectable quantity of phenols was 2 µg.

The results are given in Tables VI and VII. The hydroquinone found in some of the samples has so far not been confirmed by other methods and is quite uncertain. In sample 5, the 2,4-xylenol and the 3-cresol were not found by gas chromatography. However, 3 unknown substances were demonstrated in the gas chromatogram and it is possible that 2 of these unknown substances were identical with the phenols that caused these spots in paper chromatography.

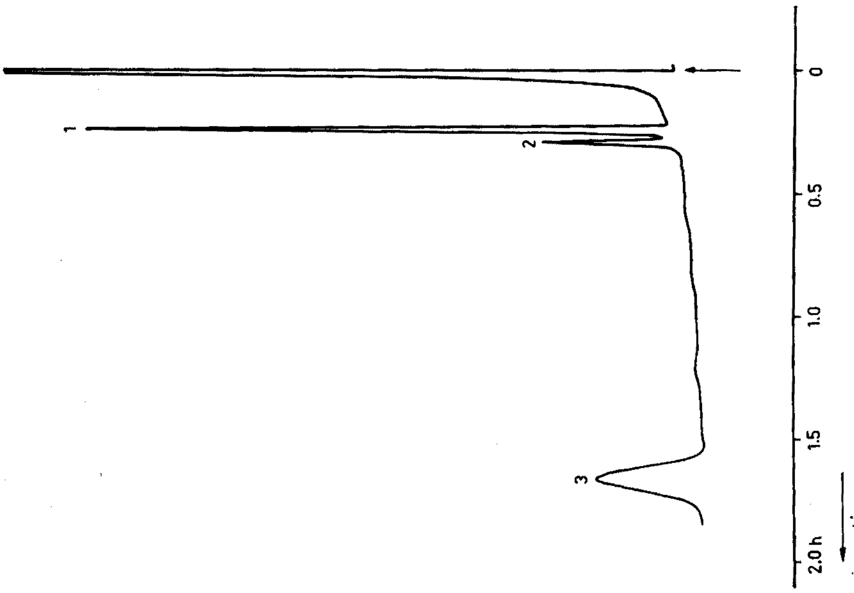


Fig. 3. Gas chromatogram of the phenols in sample 2. Injection 2 µl. (1) phenol, (2) 2-cresol, (3) trichlorophenol.

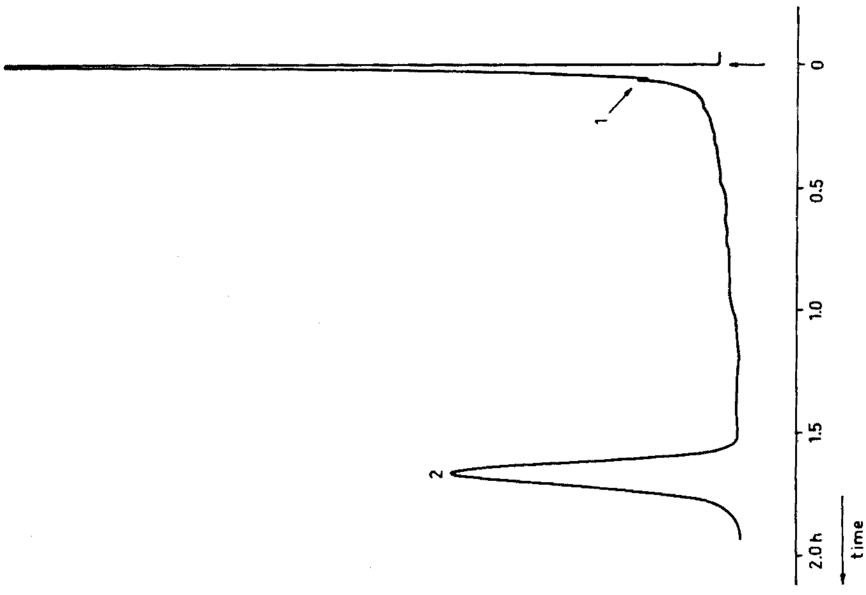


Fig. 4. Gas chromatogram of the phenols in sample 3. Injection 5 µl. (1) *p*-quinone?, (2) trichlorophenol.

TABLE V

IDENTIFICATION OF PEAKS IN DIFFERENT SAMPLES

Sample	*Peak*	*Retention time (min)*		*Phenols identified*
		Found	*Standard*	
1[a]	1	14.89	14.81	Phenol
	2	17.89	17.59	2-Cresol
	3	25.26	24.74	3-Cresol
	4	27.89	27.74	2,4-Xylenol
	5	44.21	43.61	2,4-Dichlorophenol
2	1	14.89	14.81	Phenol
	2	17.59	17.59	2-Cresol
	3	100.30	101.13	2,4,6-Trichlorophenol
3	1	3.34	3.38	*p*-Quinone?
	2	100.45	101.13	2,4,6-Trichlorophenol
4	1	15.41	15.33	Phenol
	2	18.65	18.64	2-Cresol
	3	26.02	26.01	3-Cresol
	4	28.95	29.02	2,4-Xylenol
5	1	12.03		?
	2	14.96	14.81	Phenol
	3	21.28		?
	4	37.74		?
	5	101.13	101.13	2,4,6-Trichlorophenol
6	1	13.13	13.20	Phenol
	2	15.56	15.90	2-Cresol?
7	1	4.69		?
	2	6.84	6.82	Guaiacol?
	3	8.90		?
	4	11.03		?
	5	13.22	13.20	Phenol
	6	15.81	15.90	2-Cresol
	7	22.22	22.22	3-Cresol
	8	24.51	24.26	2,4-Xylenol
	9	39.00	39.30	2,4-Dichlorophenol
	10	51.53		?
	11	83.44		?
	12	89.72	91.06	2,4,6-Trichlorophenol

[a] Sample 1 was from the same source as sample 2, but the exact quantity of water from which it was prepared was not known.

Ultraviolet spectrophotometry

The difference spectrum between the phenol and the phenolate was measured as described by WEXLER[15]. The residue containing the phenols was dissolved in 25 ml of methanol. From this solution two aliquots of 10 ml were taken. The first portion was diluted to 25 ml with methanol. To the second portion 12.5 ml of a 2 *M* solution of potassium hydroxide in methanol was added and the mixture was diluted to 25 ml with methanol. The difference spectrum was measured using a Beckman recording D.B. spectrophotometer. The wavelengths of maximum absorbance of standard solutions of phenols are given in Table VIII together with the approximate molar extinction coefficient for the maximum in the neighbourhood of 300 mμ.

TABLE VI

R_F VALUES OF PHENOLS

Component	R_F	*Component*	R_F
Phenol	0.02	2-Cresol	0.62
4-Ethylphenol	0.35	4-Cresol	0.62
Guaiacol	0.36	2,4-Dichlorophenol	0.65
Hydroquinone	0.43	4-Chlorophenol	0.68–0.70
2,4-Xylenol	0.50	2-Nitrophenol	0.70–0.72
2,5-Xylenol	0.55	2,4,6-Trichlorophenol	0.78
3-Cresol	0.60		

TABLE VII

PHENOLS FOUND BY PAPER CHROMATOGRAPHY

Sample	R_F	*Phenols identified*
1	0.02	Phenol
	0.43	Hydroquinone?
	0.60	3-Cresol
	0.65	2,4-Dichlorophenol
2	0.02	Phenol
	0.77	2,4,6-Trichlorophenol
3	0.76–0.77	2,4,6-Trichlorophenol
4	0.02	Phenol
	0.39–0.40	Hydroquinone?
	0.62	2- or 4-Cresol
5	0.02	Phenol
	0.52	2,4-Xylenol?
	0.60	3-Cresol?
	0.78	2,4,6-Trichlorophenol

TABLE VIII

MAXIMUM ABSORBANCE WAVELENGTH AND MOLAR EXTINCTION COEFFICIENTS

	λ_{m1} (*mμ*)	λ_{m2} (*mμ*)	α_m *at* λ_{m2} ($l\ mol^{-1} cm^{-1}$)
Phenol	240	295	2450
2-Cresol	240	292	3350
3-Cresol	242	292	2900
4-Cresol	242	298	3300
2,4-Xylenol	255	300	3800
2,4-Dichlorophenol	250	310	5300
2,4,6-Trichlorophenol	250	318	5300
p-Quinone	218,275	315	2200

In general, the sum of the phenols was measured by this method. However, the chlorophenols showed maximum absorbance at wavelengths differing by 15–20 mμ from that of phenol and the methylphenols, and the response of one group of phenols at the maximum of the other group was small. The distance between the two maxima was not large enough to permit a quantitative determination when the two groups were present in amounts giving a large difference in absorbance at the respective maxima.

Sample 3 containing trichlorophenol exhibited a maximum at 318 mμ as expected. The presence of *p*-quinone could not be confirmed in this way, because the concentration was too low. With sample 2 it was derived, from the gas chromatogram, that the proportion of the concentrations of trichlorophenol, phenol and 2-cresol was approximately 8:3:1. The ultraviolet spectrum of the sample was compared with an artificial mixture of the same composition. The sample as well as the synthetic mixture gave the maximum of trichlorophenol and a particularly shaped "shoulder" caused by phenol and 2-cresol.

Infrared spectroscopy

The complex mixtures of phenols, containing apart from the phenols and chlorophenols already identified by gas and paper chromatography, many other more complicated phenols and their chlorination products, gave infrared spectra which

TABLE IX

SUMMARY OF RESULTS BY THE DIFFERENT METHODS

Sample	*G–L chrom.*	*Paper chrom.*	*UV.*	*IR.*
1	Phenol 2-Cresol 3-Cresol 2,4-Xylenol 2,4-Dichlorophenol	Phenol 3-Cresol 2,4-Dichlorophenol Hydroquinone?		
2	Phenol 2-Cresol 2,4,6-Trichlorophenol	Phenol 2,4,6-Trichlorophenol	Phenol Chlorophenol	Aromatic OH methyl polychlorinated compound
3	2,4,6-Trichlorophenol *p*-Quinone?	2,4,6-Trichlorophenol	Chlorophenol	Aromatic OH methyl polychlorinated compound
4	Phenol 2-Cresol 3-Cresol 2,4-Xylenol	Phenol 2- or 4-Cresol Hydroquinone?		Aromatic OH methyl dimethyl
5	Phenol 2,4,6-Trichlorophenol 3 peaks unidentified	Phenol 2,4,6-Trichlorophenol 2,4-Xylenol? 3-Cresol?		Aromatic OH polychlorinated compound methyl
6	Phenol 2-Cresol			Aromatic OH methyl
7	Phenol 2-Cresol 3-Cresol 2,4-Xylenol 2,4-Dichlorophenol 2,4,6-Trichlorophenol Guaiacol? 5 peaks unidentified			

were difficult to interpret. The height of the characteristic peaks was influenced not only by the concentration of the expected substances, but also by the presence of unknown, probably closely related substances. The spectra of solutions of the phenolic residues in chloroform or benzene were measured against the solvent and compared with data obtained from the literature and with the spectra of the pure substances and mixtures of these substances. The conclusions as a whole confirmed the results found by the other methods; they are summarized together with the data obtained by the other methods in Table IX.

Determination of the individual phenols and chlorophenols

Paper chromatography and infrared spectroscopy give no quantitative information, whereas ultraviolet spectrophotometry yields only the total of the phenols and chlorophenols, and so gas–liquid chromatography remains the most promising method for quantitative work. Experiments were carried out with phenol in the following way. Solutions of phenol were prepared in concentrations varying from 0.8 to 8 mg/ml. For the injection of 2.5–5 μl, the 10-μl syringe was filled in the sequence: some air, some benzene, again some air, then the sample and finally more air. The length of the sample column was read. This method had the advantage that corrections for the portion remaining in the needle and for evaporation were not necessary[35]. The measurements were performed under the same conditions as before except that the paper speed was higher (2400 mm/h) to obtain broader peaks better adapted for quantitative work.

When the peak height per unit of injection volume was plotted against concentration, the curve was nearly straight from 1.6 to 8 mg/ml. This corresponded to peak heights from 5 to 10 cm. A plot of peak area per unit of injection volume against concentration gave a very slightly curved line, equally curved over the whole range. In both cases the deviations from direct proportionality were so small that they could be neglected. Errors arising from other sources, particularly the adsorption and desorption procedure and the separation of phenols from other organic substances, were probably larger.

By measurement of the peak heights of the chromatogram of sample 2 the content of the sample was found in μg/l: phenol 5.9, 2-cresol 1.8 and trichlorophenol 14. This amounted to 55% of the total amount of phenols. In sample 3, both peak height and peak area were measured; both gave a trichlorophenol content of nearly 6 μg/l, which was about 30% of the total phenol content. It must be emphasized that these values were only fairly rough estimations and that the recovery of individual phenols with the other samples was lower—only a few per cent of the phenolic group. It is probable that chlorocresols and more complicated phenols and chlorophenols which for the greater part were not found in the gas-chromatographic procedure applied caused the low recovery. This is in accordance with the finding of small unknown peaks in the chromatogram of some of these samples.

However, mixtures of simple phenols and chlorophenols could be determined with reasonable precision and accuracy as was shown in determining the losses by evaporation in the separation procedure. When the concentration of the substances was high enough (in the mg/l range), the adsorption procedure could be replaced by an extraction procedure followed as usual by separation from other organic compounds if present. This separation was always necessary, for components from the acid and neutral groups also gave peaks in the chromatogram under the same conditions. The separation had to be carried out with a minimum amount of organic substances of 50 mg and preferably with 500–1000 mg; otherwise the losses caused by adhesion and adsorption to the walls of the vessels could be excessive.

The method was capable of determining simple phenols in small quantities in process and industrial waste water as well as in surface and drinking water.

SUMMARY

After concentration of the organic substances from water samples of 700 to 20,000 l by adsorption on active carbon and desorption with chloroform in a large Soxhlet apparatus, the organic compounds were separated by extraction into 5 different groups: acids, phenols, bases, neutral and amphoteric substances. The phenol group was investigated by gas and paper chromatography, ultraviolet difference spectrophotometry and infrared spectroscopy. Phenol, 2,4,6-trichlorophenol, 2- and 3-cresol, 2,4-xylenol and 2,4-dichlorophenol were identified in samples of raw and treated water. Quantitative measurements proved to be possible with gas chromatography. The conditions for quantitative desorption and separation were studied.

RÉSUMÉ

Les auteurs proposent une méthode pour concentrer, séparer et analyser des substances organiques dans des échantillons de 700 à 20,000 l d'eau. On procède par adsorption sur charbon actif et désorption avec chloroforme dans un grand appareil de Soxhlet, puis à une séparation par extraction en 5 groupes: acides, phénols, bases, substances neutres et amphotères. Les phénols sont examinés par chromatographie gazeuse et chromatographie sur papier, spectrophotométrie dans l'ultraviolet et spectroscopie infrarouge. Phénol, 2,4,6-trichlorophénol, 2- et 3-crésols, 2,4-xylénol et 2,4-dichlorophénol ont été identifiés dans l'eau.

ZUSAMMENFASSUNG

Nach Konzentration der organischen Substanzen aus Wasserproben durch Adsorption an Aktivkohle und Desorption mit Chloroform in einer grossen Soxhlet-Apparatur wurden die organischen Verbindungen durch Extraktion in 5 Gruppen getrennt: Säuren, Phenole, Basen, neutrale und amphotere Substanzen. Die Phenolgruppe wurde mit der Gas- und Papierchromatographie, der Ultraviolettdifferenzspektralphotometrie und Infrarotspektroskopie untersucht. Phenol, 2,4,6-Trichlorophenol, 2- und 3-Kresol, 2,4-Xylenol und 2,4-Dichlorophenol wurden in rohen und behandelten Wasser identifiziert.

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THE DETERMINATION OF VANADIUM IN SEA AND NATURAL WATERS, BIOLOGICAL MATERIALS AND SILICATE SEDIMENTS AND ROCKS

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Interest in the marine chemistry of vanadium has quickened in the last few years since the discovery that certain Ascidians and Tunicates have an organo-vanadium compound as a respiratory pigment. Several determinations of the element in sea water have been described recently; these are listed in Table I together with earlier data. The data are too sparse for one to be able to determine whether these variations are real and brought about by biological or geochemical processes, or whether, as seems more probable, they are caused by the use of inaccurate analytical methods.

TABLE I

PUBLISHED DETERMINATIONS OF VANADIUM IN SEA WATER

Concentration found ($\mu g/l$)	*Method of concentration*	*Method of determination*	*Reference*
0.2–0.4	Coprecipitated with iron(III) hydroxide	Spectrographic	1
0.5	Coprecipitated	Spectrographic	2
2.4–7.0	Coprecipitated with tannin + thionalide + oxine + Fe^{3+} + Al^{3+}	Spectrographic	3
2.1–4.6	Coprecipitated with iron(III) cupferrate	Photometric as phosphotungstate	4,5
1.7–2.8	Coprecipitated with iron(III) hydroxide	Photometric as oxinate	6–8
0.63	Extracted as diethyl dithioammonium carbamate	Spectrographic	9
1.0	Coprecipitated with iron(III) hydroxide	Polarographic	10

Both solvent extraction[11-13] and coprecipitation techniques[14,15] have been used for the concentration of vanadium from other natural waters. In most methods the determination was completed spectrographically, but NAITO AND SUGAWARA[7] have described a photometric method.

Most of the vanadium determinations reported for silicate rocks appear to have been carried out spectrographically, with or without preliminary concentration. Only comparatively few photometric methods for the determination of the element in these materials have been described. For the opening up of silicates before the analysis, both acid[16] and alkaline[17] attack can be employed. Generally the latter has been favoured since vanadium can be leached out of the fused cake leaving iron and a number of other elements in the insoluble residue; chromium accompanies vanadium and if present in appreciable amounts must be separated from it before photometric determination, usually by extraction with 8-hydroxyquinoline in chloroform. Vanadium is usually determined photometrically as phosphotungstovanadic acid[17] but both the 8-hydroxyquinoline and nicotinohydroxamic acid[18] complexes have also been used on account of their higher sensitivity.

The concentrations of vanadium present in biological materials are normally more than an order of magnitude lower than those at which the element occurs in silicate rocks; this has necessitated the use of preliminary concentration techniques before vanadium can be determined spectrographically[19]. The presence of iron and copper in the ash of biological samples has necessitated the use of solvent extraction[20-23] or electrolytic separation[24,25] procedures before the element can be determined spectrophotometrically or polarographically.

This paper describes the combination of an almost specific ion-exchange process with spectrophotometry to provide a simple and specific procedure for the determination of vanadium in a wide range of natural materials.

Concentration of vanadium from sea water

Since the concentration of vanadium in sea water is too low for direct determination it is necessary to concentrate it from a large volume of sample. Coprecipitation and cocrystallization are probably the simplest techniques for concentration of trace elements from sea water; both techniques have been used for vanadium (see Table I).

The efficiency of the various concentration procedures was therefore tested by equilibrating 3-l aliquots of sea water with vanadium-48, treating them with solutions of salts of readily hydrolysable metals and bringing them to suitable pH values. After coagulation of the hydroxide it was filtered off and dissolved in hydrochloric acid and the percentage coprecipitation was assessed by liquid scintillation counting. An analogous coprecipitation with hydrous manganese dioxide was made by treating the sample with potassium permanganate and ethanol. The cocrystallization of vanadium with 5,7-dibromo-8-hydroxyquinoline, and with thionalide was also investigated. Aliquots (3 l) of sea water containing ^{48}V were treated with acetone solutions of the reagents, and the resultant precipitates were filtered off. The precipitates were dissolved in nitric acid and the percentages of vanadium cocrystallized were estimated by radiometry. A coprecipitation was also made from sea water as described by BLACK AND MITCHELL[3] using tannin, thionalide and 8-hydroxyquinoline both alone and in the presence of iron and aluminium.

The results of these experiments (Table II) showed that vanadium was quantitatively coprecipitated by the hydroxides of iron and chromium and by hydrous manganese dioxide. Coprecipitation with aluminium hydroxide was incomplete at all pH values. Cocrystallization with both 5,7-dibromo-8-hydroxyquinoline and thionalide was ineffective.

The mixed tannin + thionalide + 8-hydroxyquinoline reagent alone precipitated vanadium fairly effectively; in the presence of iron and aluminium the coprecipitation was complete, but the slimy precipitate was difficult to filter and wash and the use of this procedure was not investigated further.

TABLE II

COPRECIPITATION AND COCRYSTALLIZATION OF VANADIUM FROM 3 l OF SEA WATER

Reagent	*Weight used*	*% Carried*
Iron(III) chloride	60 mg Fe	100
Aluminium sulphate	60 mg Al	80[a]
Chromium(III) nitrate	60 mg Cr	100[b]
Permanganate + ethanol	50 mg Mn	100[c]
Thionalide	300 mg	15
Dibromo-oxine	250 mg	9
Tannin + thionalide + oxine	—	93
Tannin + thionalide + oxine + Fe^{3+} + Al^{3+}	—	100

[a] At pH 8.5.
[b] At pH 6.5 (maximum coprecipitation).
[c] At pH 3.2–5.3.

Coprecipitation with iron was selected for further study since the precipitate of iron(III) hydroxide settled quickly and was easy to filter and dissolve.

Coprecipitation of vanadium by iron(III) hydroxide

The effect of pH on the coprecipitation of vanadium by iron(III) hydroxide was investigated radiochemically. Aliquots of sea water (2 l) equilibrated with *ca.* 0.04 μc of ^{48}V were acidified with dilute hydrochloric acid and iron(III) chloride solution (equivalent to 20 mg of iron) was added. The samples were adjusted to a series of pH values by addition of ammonia or hydrochloric acid. After the precipitate of hydroxide had settled, it was filtered off and dissolved in hot hydrochloric acid. The ^{48}V activity of the solution was then measured and the percentage of vanadium coprecipitated was assessed. It was found (Table III), in agreement with the findings of KUWAMOTO[26], that coprecipitation was quantitative in the pH range *ca.* 4.0–7.5; both above and below this range the recovery decreased markedly. In all subsequent work the coprecipitation was carried out at a pH value of between 5 and 6.

TABLE III

COPRECIPITATION OF VANADIUM WITH IRON(III) HYDROXIDE AT VARIOUS pH VALUES

pH	1.4	2.1	3.2	4.5	5.1	5.7	6.2	7.1	7.5	8.0	8.5	8.9
% Coprecipitated	2	54	99	99	100	100	100	100	100	99	95	93

The recovery of the vanadium present in sea water depends markedly on the amount of iron used for coprecipitation below *ca.* 7.5 mg Fe/l (*e.g.* with 1 mg Fe/l the recovery was only 58%). With 10 mg of iron/l the recovery was complete. For the recovery of vanadium from sea water 10 mg of iron/l was therefore employed; with this amount of iron the hydroxide precipitate settled in about 12 h. It is advisable to filter the iron(III) hydroxide precipitate and dissolve it in acid as soon as possible after this time has elapsed since it becomes progressively more difficult to dissolve as it ages.

Vanadium can also be coprecipitated quantitatively from non-saline natural waters with iron(III) hydroxide at pH 5–6, but since the flocculation is a very slow process in the absence of salts it is essential to add to the sample 1 g of sodium chloride per litre before carrying out the coprecipitation.

Ion-exchange separation of vanadium from iron

Iron interferes seriously in most photometric methods for the determination of vanadium and it is therefore necessary to remove it and other interfering elements before photometry. It was thought that the separation could be achieved most simply by ion exchange. JANOUŠEK[27] has used hydrogen peroxide to elute vanadium from a column of the cation exchanger Katex FN in the analysis of the ash of fuel oil. Later, FRITZ AND ABBINK[28] separated vanadium from most other ions by eluting it from a cation-exchange column with a 1% solution of hydrogen peroxide in 0.01 *M* sulphuric acid. The use of hydrogen peroxide for the elution of microgram amounts of vanadium was therefore investigated.

In order to determine the optimum conditions for the separation, 200-μg portions of vanadium (as vanadate) equilibrated with 0.04 μc of ^{48}V were adsorbed on 8 cm × 0.8 cm diameter columns of Zeo-Karb 225 resin (8% cross-linked, 52–100 mesh). The columns were repeatedly eluted with 10-ml aliquots of hydrogen peroxide of various strengths; the amount of vanadium contained in each eluate was estimated by scintillation counting. The results of these experiments (Table IV) showed that the ease of elution of the vanadium depended on the peroxide concentration. However, at the higher concentrations some decomposition of the peroxide occurred and the oxygen formed tended to cause channelling in the column; for this reason, 40 ml of 0.3% hydrogen peroxide solution was used in all subsequent work.

TABLE IV

PERCENTAGE ELUTION OF VANADIUM WITH 10-ml ALIQUOTS OF VARIOUS STRENGTHS OF HYDROGEN PEROXIDE

Strength of peroxide (%, w/v)	*0.06*	*0.3*	*0.6*	*1.5*
Eluate number				
1	1	1	67	82
2	42	95	28	15
3	35	3	4	3
4	18	1	1	—
5	4	—	—	—
Total	100	100	100	100

The behaviour of a number of metals adsorbed on the ion-exchange column to elution by up to 250 ml of 0.3% hydrogen peroxide was examined. It was found that iron (50 mg Fe^{3+}), aluminium (5 mg), cobalt, zinc, titanium (2.5 mg each) and uranium and cerium (1 mg each) were not eluted. The exchange capacity of the column used (150 meq.) is sufficiently large to retain the cations from 50-mg samples of silicate rocks; it is therefore possible to use the column for the separation of the vanadium from most of the other elements present in a solution obtained by digestion of the rock with hydrofluoric and perchloric acids.

Photometric determination of vanadium

The photometric diaminobenzidine method of CHENG[29] was selected for the determination of vanadium because of its specificity and fairly high sensitivity. Tests were made using the conditions recommended by CHENG and it was found that the results were reproducible and that Beer's law was obeyed up to a vanadium concentration of at least 250 μg/25 ml. No interference was produced by 1-mg amounts of Cu^{2+}, Fe^{3+}, Mn^{2+}, Zn^{2+}, Pb^{2+}, Mo^{6+}, W^{6+} or Se^{4+}. Since oxidizing agents produce coloured compounds with this reagent it is essential that all the hydrogen peroxide present in the eluate from the ion-exchange process should be destroyed before the determination of vanadium is attempted. This can be readily accomplished by evaporating the eluate to dryness in a platinum basin.

EXPERIMENTAL

Apparatus

A Unicam S.P.500 spectrophotometer was used for all spectrophotometric measurements. Measurements of ^{48}V activity were made by means of a NaI(Tl) well-crystal used in conjunction with an EKCO N664A scintillation counter and EKCO N530F scaler.

Reagents

Iron(III) chloride solution. Dissolve 0.5 g of "Specpure" iron sponge in 10 ml of concentrated nitric acid. After dissolution, add 15 ml of concentrated hydrochloric acid and evaporate the solution to small volume. Dilute to 500 ml with 0.05 *N* hydrochloric acid; this solution contains 1 mg Fe/ml.

Hydrogen peroxide 0.3%. Dilute 10 ml of 30%(w/v) hydrogen peroxide solution to 1 l.

Diaminobenzidine reagent. Dissolve 0.1 g of 3,3'-diaminobenzidine in 25 ml of water. Prepare the reagent freshly as required.

Standard vanadium solution. Dissolve 0.2256 g of ammonium vanadate AR in water and dilute to 1 l. This stock solution contains 100 μg V/ml and is used for preparing the working standard solution which contains 2 μg V/ml.

Ion-exchange resin. Zeo-Karb 225 (8% cross-linked, 52–100 mesh) cation-exchange resin was washed several times with warm 3 *N* hydrochloric acid and then with water. An 8-cm column of resin was packed into a 0.8-cm diameter ion-exchange tube and thoroughly washed with water. After use, the ion exchanger was regenerated with 300 ml of 3 *N* hydrochloric acid and washed with 200 ml of water.

Determination of vanadium in sea water and natural waters

Place 3 l of the filtered sample (0.5-μ filter) in a 5-l conical flask (if the sample is a fresh water of low salinity treat it with 3 g of sodium chloride), add 15 ml of 1 *N* hydrochloric acid and 30 ml of iron(III) chloride solution. Using indicator paper, adjust the pH to 5–6 with 4 *N* ammonia solution and allow the covered flask to stand overnight. Siphon the supernatant layer through a 3-cm Whatman GF/B glass-fibre filter. Centrifuge the remaining liquid containing the precipitate at 2000 *g* for 10 min and discard the clear liquid. Wash the precipitate with 30 ml of 0.5% ammonium nitrate solution, centrifuge again and discard the liquid. Dissolve the precipitate on the glass-fibre filter in 10–20 ml of warm 2 *N* hydrochloric acid and add this to the main bulk of the precipitate. Warm until the latter has dissolved.

Dilute the solution until its acidity is *ca.* 0.1 *N* and allow it to pass through the ion-exchange column. Iron and most of the metal ions will form a dark-coloured band at the top of the column. Wash the column with 50 ml of 0.1 *N* hydrochloric acid, and discard the washings. Elute vanadium with 40 ml of 0.3% hydrogen peroxide solution, collect the eluate in a platinum basin, add 2–3 drops of perchloric acid and evaporate on the water bath to destroy hydrogen peroxide and the peroxy–vanadium complex. Destroy any organic matter present by evaporating under an infrared heater until dense white fumes are evolved. Transfer the solution quantitatively to a 10-ml graduated flask using 0.05 *N* perchloric acid. Add 1 ml of 85% phosphoric acid, mix well and allow the solution to cool. Add 1 ml of diaminobenzidine reagent and dilute to volume. After *ca.* 30 min measure the optical density of the solution at 470 mμ in a 4-cm cell relative to distilled water. Carry out a reagent blank in the same manner using 3 l of sea water which has been stripped of vanadium by coprecipitation with iron(III) hydroxide; its normal optical density is *ca.* 0.015.

Calibrate the method by placing 2.5- and 5-ml aliquots of the working standard vanadium solution (5 and 10 μg V respectively) in 10-ml graduated flasks and adding 1 ml of 85% phosphoric acid and 1 ml of diaminobenzidine reagent and diluting to 10 ml. After 30 min measure the optical density at 470 mμ in a 4-cm cell. Carry out a reagent blank in the same way using distilled water.

Determination of vanadium in silicate rocks

Place 0.5 g of the powdered sample in a platinum crucible, add 4 ml of 60% (w/w) perchloric acid and 15 ml of 40% (w/w) hydrofluoric acid and heat the covered crucible overnight on the water bath. On the following morning, remove the lid and allow the hydrofluoric acid to evaporate. When no visible fumes are evolved place the crucible under an infrared heater and evaporate almost to dryness. Add 2 ml of perchloric acid, stir the crucible and repeat the evaporation. Add a further 2 ml of perchloric acid and 15 ml of water and warm the crucible on the water bath until the cake has dissolved. Transfer the solution to a 250-ml volumetric flask and dilute to volume. This solution corresponds with a double strength "solution B" of the rapid silicate analysis scheme of RILEY AND WILLIAMS[30]. Pass a 50-ml aliquot ($\ngtr$ 200 μg V) of the solution through the cation-exchange column. Wash the resin with 50 ml of 0.1 *N* hydrochloric acid and then elute vanadium with 40 ml of 0.3% hydrogen peroxide. Continue the analysis as described for sea water. Determine the reagent blank in the same manner but omitting the sample. Calibrate the method as described above for sea water.

Determination of vanadium in biological materials

Digest 2–5 g of the dried (105°) sample with concentrated nitric acid in a loosely stoppered 500-ml conical flask on the hot plate until the sample is completely oxidized, adding further nitric acid as required. When the oxidation is complete, add 3 ml of 60% (w/w) perchloric acid and evaporate until dense white fumes are evolved. Take up the residue in *ca.* 500 ml of water, warming if necessary. Remove any siliceous residue by centrifugation and then pass the solution through the ion-exchange column. Wash the column with 50 ml of water and then elute vanadium with 40 ml of 0.3% hydrogen peroxide. Determine vanadium in the eluate as described above for sea water. Run a reagent blank in the same manner but omitting the sample. Prepare a calibration curve as described for sea water.

RESULTS

Accuracy and precision of methods

Sea water. The reproducibility of the method was tested by carrying out 5 replicate analyses on 3-l aliquots of filtered sea water (a composite surface water sample from the Irish Sea); these showed an average vanadium content of 1.82 ± 0.05 µg V/l. In order to test the efficiency of recovery of vanadium 3-l aliquots of the same sea water were spiked with known amounts of vanadium and with ^{48}V and then analysed. The efficiency of the isolation process was also checked by counting of the solutions used for spectrophotometry. The results of these experiments (Table V) show that the recovery of vanadium in the spectrophotometric process averaged 98 ± 2% in good agreement with the percentage recovery found by tracer methods (average 99 ± 1%).

TABLE V

RECOVERY OF VANADIUM FROM 3-l ALIQUOTS OF SEA WATER (1.8 µg V/l) TO WHICH INCREMENTS OF VANADIUM HAD BEEN ADDED

Weight of V added (µg)	0	2.5	5.0	7.5	10.0
Weight of V found (µg)	5.4	7.8	10.4	12.6	15.1
Chemical recovery (µg)	—	2.4	5.0	7.2	9.7
Chemical recovery (%)	—	96	100	96	97
Radiochemical recovery (%)	98	99.7	99.0	100.0	99.0

Silicates. Replicate analyses (6) were carried out on 2 red clays (from Discovery Station 2911 at 35°55'N and 17°29'E and Discovery Station 3498 at 34°11'N 55°32'W); they were found to contain 56.7 ± 0.7 and 97.0 ± 0.8 µg V/g respectively after drying at 105°. A chocolate coloured deep-sea clay rich in micro-manganese nodules (Discovery Station 2966 at 48°52'N 15°00'W) gave on analysis 365 ± 2 µg V/g. As a check on the recovery of vanadium, 0.2-g samples of the red clay from Discovery Station 2911 (containing 11.2 µg V) were spiked with 10 µg of vanadium and analysed; satisfactory recoveries of vanadium were obtained (21.0 and 20.9 µg corresponding to recoveries of 9.8 and 9.7 µg of the added vanadium respectively). The U.S. Geological Survey standard granite G1 was found to contain 17.2 ± 0.8 µg V/g. The values found, mainly spectrographically, for this rock by other workers (summarised by FLEISCHER AND STEVENS[31]), show very considerable variations (11–24 p.p.m.), and FLEISCHER AND STEVENS[31] have tentatively recommended a value of "perhaps 16".

Marine plants. Replicate analyses were carried out on well washed, air dried specimens of the following sea weeds, *Fucus vesiculosus*, *Laminaria digitata* and *Ascophyllum nodosum*; they were found to contain 2.20 ± 0.05, 1.82 ± 0.03 and 0.88 ± 0.03 µg V/g, respectively. As a further test of the method 2-g samples of *F. vesiculosus* (containing 4.4 µg V) were spiked with 5 µg of vanadium. On analysis 9.2 and 9.3 µg of vanadium were found, corresponding with recoveries of 4.8 and 4.9 µg of the added vanadium.

Storage of samples

Tests were made with 500-ml aliquots of sea water, which had been filtered through a 0.5-µ membrane filter and equilibrated with ^{48}V (as vanadate). They showed that there was no loss of vanadium from samples stored in the dark for 16 days in 1-l bottles of either Pyrex glass or high-density polyethylene. A loss of *ca.* 3% occurred with 1-l soda glass bottles in this period.

SUMMARY

Vanadium was concentrated from sea and natural waters by coprecipitation with iron(III) hydroxide, and separated from iron and other elements by ion exchange, using hydrogen peroxide as a very selective eluting agent. The element was determined photometrically with diaminobenzidine. The ion-exchange process was also used to separate vanadium from other elements in the analysis of silicate rocks and marine plants. Coefficients of variation of 2.8%, 1.3% and 2.5% were found for the determination of the element in sea water, marine sediments and marine plants at levels of 1.8 μg/l, 57 μg/g and 2.2 μg/g, respectively. The U.S. Geological Survey standard granite G1 was found to contain 17.2 ± 0.9 μg V/g.

RÉSUMÉ

Les auteurs proposent une méthode de dosage du vanadium dans les eaux. Le vanadium est concentré par coprécipitation à l'aide d'hydroxyde de fer(III), et séparé par échangeur d'ions, en utilisant le peroxyde d'hydrogène comme agent d'élution très sélectif. Le vanadium est enfin dosé photométriquement à l'aide de diaminobenzidine. Ce procédé est également utilisé pour l'analyse de silicates et de plantes marines. Coefficients de variation: 2.8%, 1.3%, 2.5% de vanadium pour respectivement 1.8 μg/l, 57 μg/g et 2.2 μg/g de vanadium dans eau de mer, sédiments marins et plantes marines.

ZUSAMMENFASSUNG

Vanadin wurde durch Mitfällen mit Eisen(III)hydroxid aus See- und natürlichen Wässern angereichert und von Eisen und anderen Elementen mittels Ionenaustauscher abgetrennt. Als sehr selektives Elutionsmittel wurde Wasserstoffperoxid verwendet. Die Bestimmung des Vanadins geschah photometrisch mit Diaminobenzidin. Das Ionenaustauscherverfahren wurde ebenso zur Trennung des Vanadins von anderen Elementen bei der Analyse silikatischer Gesteine und Meerespflanzen verwendet. Bei der Bestimmung des Elements in Seewasser, Meeresablagerungen und Meerespflanzen betrugen die Variationskoeffizienten 2.8%, 1.3% bzw. 2.5%, bei Gehalten von 1.8 μg/l, 57 μg/g bzw. 2.2 μg/g. Im Standardgranit G1 wurde 17.2 ± 0.9 μg V/g gefunden.

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ETUDE ANALYTIQUE ET DOSAGE DE MICRO- ET SUBMICRO-TRACES DE MANGANESE PAR POLAROGRAPHIE INVERSE

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La mise au point d'un dosage de traces de manganèse, sensible au nanogramme, nécessite une étude approfondie. En effet l'ion Mn^{2+} ne se prête pas particulièrement bien à une détermination polarographique et le mécanisme de l'oxydo-réduction sur le mercure est plus complexe que ce n'est le cas pour le zinc et le cadmium par exemple. C'est pourquoi nous avons étudié successivement les deux étapes de ce dosage: préélectrolyse cathodique et réoxydation anodique, en faisant varier les divers facteurs dont il dépend.

PARTIE EXPÉRIMENTALE

Nomenclature

t = Température (°C), T = température (degré Kelvin), S_g = surface des gouttes (mm^2), sens. = sensibilité de l'enregistrement des courbes (μA/mm), H_m = hauteur du pic de redissolution (mm), i_m = courant maximum de redissolution du Mn = $H_m \times$ sens. (μA), E_m = potentiel de i_m (V), i_{Mn} = courant limite de diffusion de Mn^{2+} (μA), v = vitesse de balayage (V/min).

Tous les potentiels sont donnés (sauf indication spéciale) par rapport à l'électrode de AgCl saturée.

Appareillage et conditions de travail

(a) *Cellule* thermostatisée Metrohm EA 669; volume: 60 ml.

(b) *Agitation magnétique.* Moteur synchrone à 375 *t*/min, barreau de fer, dimensions: 16 mm longueur, 4 mm diamètre enrobé dans du téflon, 25 mm longueur, diamètre 6 mm.

(c) *Système de désoxygénation.* Système Metrohm qui permet d'introduire l'azote soit dans la solution, soit au-dessus de celle-ci après la désoxygénation et pendant la détermination de la courbe potentiel–courant.

(d) *Electrode indicatrice.* Electrode à goutte de mercure pendante composée d'un capillaire et d'un microdoseur Metrohm E 410, permettant d'obtenir des gouttes de diamètre déterminé et reproductible.

(e) *Electrode de référence*, soit à chlorure d'argent saturée Metrohm EA 419, soit un simple fil d'argent recouvert de AgCl. Dans ce dernier cas on évite les contaminations dues au KCl qui ne sont pas négligeables et on diminue la résistance interne de la cellule.

(f) *Polarographe.* Metrohm E 261 R, type classique. Les potentiels sont toujours donnés par rapport à l'électrode de référence.

(g) *Balayages de potentiel.* Courbes de polarisation cathodique de 0 à −2.0 V. Courbes de redissolution anodique: −1.55 V vers les potentiels moins négatifs.

(h) *Vitesse de balayage.* Le plus souvent 0.33 V/min sauf dans l'étude de ce facteur (v.p. 353).

(i) *Potentiel de préélectrolyse.* −1.55 V (électrode à AgCl saturée), −1.65 V (électrode à AgCl 0.1*N*).

(j) *Durée de la préélectrolyse.* 11 min dont 10 min avec agitation, sauf dans les études concernant ce facteur (v.p. 353).

(k) *Electrolyte de base.* LiCl p.a. (U.C.B. & Baker) et KCl suprapur Merck (sauf dans l'étude de ce facteur et dans celle du pH). V.p. 347.

(l) *Concentration et force ionique.* Electrolyte de base 0.1 *N*, force ionique 0.1 sauf dans l'étude de l'influence de l'électrolyte de base (v.p. 347) et du pH. Concentration en Mn^{2+}: le plus souvent 1.0 μg/ml sauf dans l'étude de l'influence de la surface des gouttes sur i_{Mn} (v.p. 351) et dans l'établissement des courbes d'étalonnage (v.p. 355) et dans les dosages (v.p. 357).

(m) *pH.* Les solutions ne sont pas tamponnées sauf lors de l'étude de ce facteur.

(n) *Volume de la solution.* 25 ml.

(o) *Agitation de la solution.* Toujours au cours de la préélectrolyse. Quant à la redissolution elle se fait sans agitation (sauf p. 352).

(p) *Désoxygénation.* Barbotage d'azote Carba 99.99% (sans autre purification) pendant 10 min avant la préélectrolyse et l'établissement des courbes de polarisation cathodique. Pendant la préélectrolyse, la redissolution anodique et l'établissement des courbes cathodiques, ce courant gazeux est dirigé sur la surface de la solution.

(q) *Température.* 20° sauf dans l'étude de ce facteur (v.p. 350).

(r) *Surface des gouttes de mercure.* Le plus souvent $S_g = 1.38 \pm 0.04$ mm² (sauf p. 351–353).

PRÉÉLECTROLYSE (conditions de travail: v.p. 346)

Cette opération consiste à réduire l'ion Mn^{2+} en solution sur la goutte de mercure jouant le rôle de cathode ($Mn^{2+} + 2\,e + Hg \rightarrow Mn(Hg)$). Ce phénomène dépend de nombreux facteurs dont les principaux sont l'agitation, la nature de l'électrolyte de base, le pH, l'oxygène dissous dans la solution, la température, la surface de la goutte de mercure. Pour examiner ce comportement nous avons établi les courbes de polarisation avec le polarographe Metrohm mais en présence d'une agitation et sur une goutte fixe (pendante).

Rôle de l'électrolyte de base

Les sels suivants ont été examinés: LiCl, KCl, citrate de sodium, acétate de sodium, $NaClO_4$, tartrate Na-K, NH_4Cl/NH_3, K_2SO_4, KNO_3 et $Ca(NO_3)_2$.

Lorsque les vagues du Mn^{2+} et du cation de l'électrolyte de base sont bien séparées, $E_{\frac{1}{2}}$ est de -1.48 ± 0.01 V. C'est le cas pour KNO_3, K_2SO_4, $NaClO_4$, CH_3COONa, le tartrate Na-K, LiCl et KCl. Par contre le tampon ammoniacal n'est pas à recommander; $Ca(NO_3)_2$ et citrate de sodium sont inutilisables les vagues étant superposées. Dans les cas où les vagues sont distinctes on constate que pour des concentrations $(Mn^{2+}) = 1$ μg/ml, le début de vague se trouve à -1.40 ± 0.02 V, et le potentiel de début de palier à -1.55 ± 0.03 V. Quant au courant i_{Mn} (déduction faite de celui de l'électrolyte de base) il est donné dans le Tableau I.

Nous utiliserons comme électrolyte de base dans la suite de ce travail (sauf dans des cas particuliers) soit LiCl, soit KCl. L'emploi des sels quaternaires n'apporte pas d'amélioration. Quant au tampon TRIS il est inutilisable car il masque la vague de Mn^{2+}.

TABLEAU I, RÔLE DE L'ÉLECTROLYTE DE BASE

Electrolyte de base	i_{Mn} *(µA)*	*pH*
LiCl	0.59	7.26
KNO_3	0.46	7.26
$NaClO_4$	0.46	7.35
KCl s.p.	0.40	5.92
KCl p.a.	0.40	6.43
CH_3COONa	0.45	7.77
K_2SO_4	0.38	7.23
Tartrate Na-K	0.34	7.23

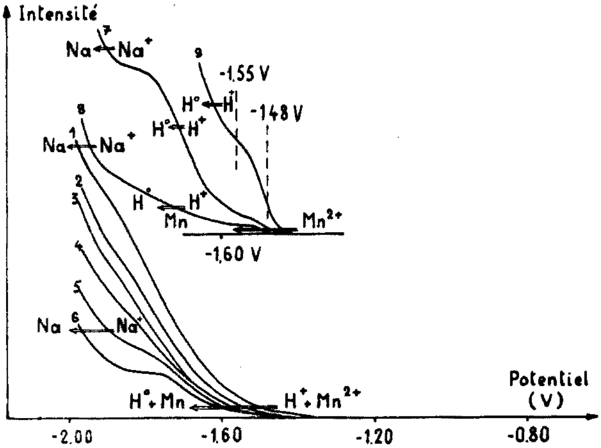

Fig. 1. Courbes potentiel–courant en fonction du pH. Courbes 1–6, sens. 1.00 µA/mm; 7–8, sens. 0.20 µA/mm; 9, 0.02 µA/mm.

TABLEAU II, RÔLE DU pH

Courbe	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
pH	5.14	5.33	5.53	5.74	6.05	6.38	6.72	8.15	8.15

Rôle du pH

Nous avons préparé des solutions CH_3COOH/CH_3COONa de divers pH. Les courbes de polarisation qui en résultent sont données dans la Fig. 1. La valeur du pH pour chaque courbe de polarisation est donnée dans le Tableau II. On remarque qu'aux pH < 6, la vague du Mn^{2+} est complètement masquée par celle du proton. Pour $6 <$ pH < 7 il y a interférence et pour pH > 7 la vague du manganèse est aisément mesurable. (Les remarques sur l'effet de la concentration d'oxygène sur le dosage peuvent aussi s'appliquer au proton.) Comme prévu le début du palier de diffusion du Mn^{2+} est situé aux environs de -1.55 V. Afin de s'assurer que ce potentiel est bien celui que nous devons choisir pour effectuer la préélectrolyse, nous avons étudié le comportement du proton dans ces conditions. Pour cela nous avons mesuré le courant de la solution tampon seule à divers pH et ce même courant après avoir ajouté 1.0 μg/ml d'ion Mn^{2+}. Les résultats sont donnés dans la Fig. 2. i_{Mn} correspond à la hauteur de la vague du Mn^{2+} à -1.55 V. On remarque dans la zone hachurée, la vague de l'ion Mn^{2+} est masquée par celle du proton. Il est donc impossible de faire un dosage aux $pH < 5.80$, même pour des teneurs en Mn^{2+} de l'ordre du μg/ml.

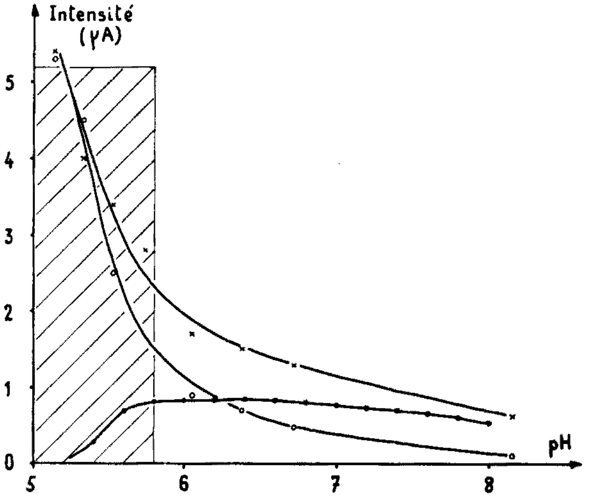

Fig. 2. Influence du pH sur i_{Mn}. ○, solution tampon seule: i_1; ×, solution tampon + 1.0 μg/ml d'ion Mn^{2+}: i_2; ●, i_2-i_1.

Influence de l'oxygène dissous (Electrolyte de base: LiCl 0.1 *N*)

On fait barboter l'azote Carba 99.99% ou l'azote technique 99.5% (sans purification) pendant 10 à 15 min dans la solution homogénéisée par agitation, puis le courant est dirigé au moyen d'un robinet à 2 voies, à la surface de la solution. On maintient une légère surpression de N_2 et évite ainsi tout contact avec l'atmosphère. Dans ces conditions on constate qu'avec l'azote Carba 99.99% la vague d'O_2 correspond à une teneur en $O_2 \leqslant 10$ ng/ml, et qu'avec l'azote technique $(O_2) \leqslant 180$ ng/ml (voir Fig. 3).

L'emploi du sulfite pour l'élimination de l'oxygène dissous n'est pas à recommander, d'une part parce que la désoxygénation n'est pas quantitative*, elle n'est pas supérieure à celle qu'on obtient avec l'azote technique. De plus on introduit avec le sulfite des impurités métalliques qui gênent la détermination lorsque les quantités de manganèse sont de l'ordre du nanogramme.

Nous devons remarquer qu'une substance qui se réduit sur la goutte de mercure peut gêner un dosage polarographique par superposition des vagues même si elle ne forme pas d'amalgame. Cet effet perturbateur ne se fait pas trop sentir sur la réoxydation anodique. Nous avons montré par exemple dans la suite de ce travail que l'oxygène ne gêne pas le dosage du nanogramme de Mn^{2+} si $(O_2) \leqslant 10$ ng.

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* et que d'autre part

Influence de la température (Electrolyte de base: LiCl 0.1 N; précision des températures: ±0.2°)

Chaque valeur du Tableau III représente la moyenne de 3 mesures sur des gouttes différentes. On observe une très bonne reproductibilité de $E_{\frac{1}{2}}$ qui se déplace vers des potentiels moins négatifs lorsque la température augmente. Nous avons déterminé la fonction $E_{\frac{1}{2}} = f(T)$; c'est une droite de formule:

$$E_{\frac{1}{2}} = 8.0 \cdot 10^{-4}T - 1.72$$

i_{Mn} augmente rapidement avec T (de 1 à 4 entre 20 et 80°). Quant à la précision, elle est un peu plus faible aux températures élevées. Nous verrons par la suite que la

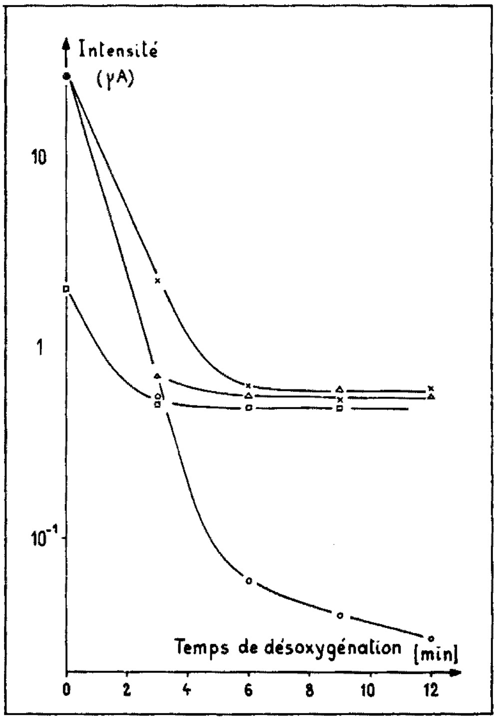

Fig. 3. Désoxygénation avec N_2 99.5%. ×, intensité mesurée à −1.40 V; □, i_{Mn}. Désoxygénation avec N_2 99.99%. ○, intensité mesurée à −1.40 V; △, i_{Mn}.

TABLEAU III, INFLUENCE DE LA TEMPÉRATURE

Température (°C)	$E_{\frac{1}{2}}$ *(V)*	$i_{Mn^{2+}}$ *(μA)*	$i_{Mn^{2+}}$ *erreur extrême (%)*
20	−1.480±0.004	0.45±0.03	± 6.7
30	−1.465±0.003	0.53±0.07	13.2
40	−1.456±0.000	0.70±0.06	8.6
50	−1.449±0.002	0.99±0.16	16.2
60	−1.439±0.002	1.15±0.15	13.0
70	−1.434±0.004	1.60±0.20	12.5
80	−1.424±0.008	1.94±0.33	17.0

méthode est suffisamment sensible pour qu'il ne soit pas nécessaire d'avoir recours à ces dernières.

Influence de l'agitation

Pour déterminer l'importance de l'agitation sur la réduction du Mn^{2+}, nous avons établi les courbes de polarisation avec et sans agitation dans les conditions indiquées à la p. 346, solution de base LiCl 0.1 *N*. On remarque que si la solution n'est pas agitée, il se produit un maximum qu'il est difficile d'éliminer avec la gélatine et le courant $i_{Mn} = 0.052 \pm 0.015$ μA est environ 10 fois plus faible que lors de l'agitation. Il est donc indispensable d'agiter pendant la préélectrolyse et toujours dans les mêmes conditions (v.p. 346).

Influence de la surface de la goutte

Au moyen du microdoseur Metrohm E 410 on peut obtenir des gouttes de mercure de surface bien déterminée et reproductible. Cette Maison donne pour chaque division du microdoseur, le diamètre, la surface ainsi que l'erreur en % sur la surface de la goutte. Nous avons reporté ces données ainsi que les valeurs de i_{Mn} obtenues dans le Tableau IV. Les essais ont été faits dans les conditions données à la p. 346 avec $(Mn^{2+}) = 0.5$ μg/ml. Electrolyte de base: LiCl 0.1 *N*. Pour chaque surface de goutte, 5 déterminations ont été faites qui nous ont permis d'apprécier la reproductibilité du microdoseur. Elle correspond bien aux valeurs données par le fournisseur. L'augmentation de i_{Mn} avec la surface de la goutte n'est pas rigoureusement proportionnelle. Il est donc indispensable d'obtenir des gouttes de dimension déterminée et reproductible: ce dispositif le permet.

TABLEAU IV, INFLUENCE DE LA SURFACE DE LA GOUTTE SUR i_{Mn}

Divisions du microdoseur	*Diamètre de la goutte (mm)*	*Surface de la goutte (mm²)*	*Erreur % sur surf.*	i_{Mn} (μA)
4	0.83	2.22 ± 0.07	3.15	0.31
3	0.76	1.80 ± 0.05	2.78	0.26
2	0.66	1.38 ± 0.04	2.90	0.21
1	0.52	0.86 ± 0.03	3.49	0.17

Etude du rapport $(Mn^{2+})/i_{Mn}$

Conditions de travail: v.p. 346 sauf pour la concentration en manganèse qui est de 0.1 et 1 μg/ml. Electrolyte de base: LiCl 0.1 *N*. Pour chacune des 2 concentrations nous avons effectué 5 essais complets. Nous avons calculé la constante *K* de l'équation $i_{Mn} = K(Mn^{2+})$ au moyen des valeurs obtenues:

$$K = 0.504 \pm 0.046 \ (0.1\ \mu\text{g Mn/ml})$$

$$K = 0.508 \pm 0.038 \ (1.0\ \mu\text{g Mn/ml})$$

PRÉÉLECTROLYSE ET OXYDATION ANODIQUE (POLAROGRAPHIE INVERSE)

Dans la première partie de ce travail nous avons étudié la réduction du Mn^{2+} sur l'électrode à goutte suspendue dans une solution agitée. Les courbes de polarisation ont été établies dans diverses conditions ce qui nous a apporté les renseignements utiles concernant la thermodynamique et la cinétique de cette réaction et nous a permis d'en déterminer les conditions optimums. Il s'agit maintenant d'examiner le comportement du manganèse métallique dissous dans le mercure lorsque, partant du potentiel de préélectrolyse, on applique à la goutte un potentiel de moins en moins négatif (balayage anodique). Les courbes des Fig. 4 et 5 permettent de suivre ce phénomène.

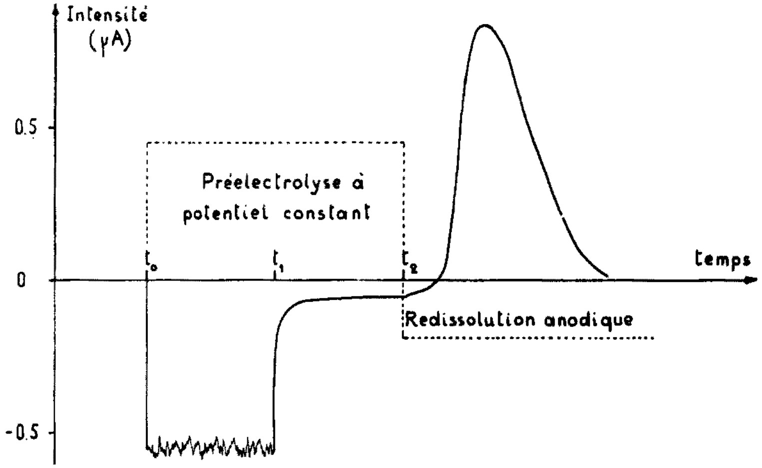

Fig. 4. Variation du courant dans les différentes phases de la méthode. t_0, début de la préelectrolyse; t_1, arrêt de l'agitation; t_2, début du balayage anodique; $t_1 - t_0$, durée de la préelectrolyse en solution agitée; $t_2 - t_1$, durée de la préelectrolyse en solution non agitée.

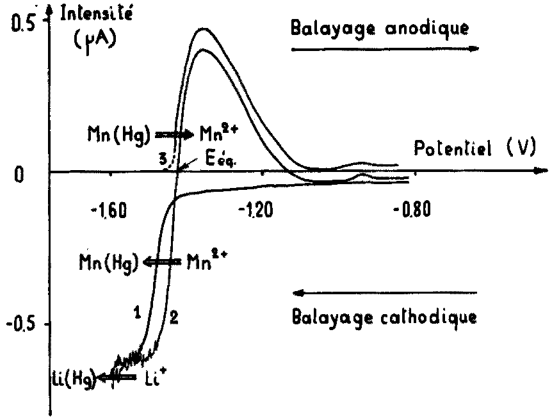

Fig. 5. Courbes potentiel–courant en solution agitée. (1) représente la courbe de polarisation résultante sur goutte de mercure pure suspendue; balayage de potentiel de 0 à −2.0 V; (2) représente la courbe de polarisation résultante sur goutte de mercure pure suspendue; balayage de potentiel de −1.60 à 0 V; (3) est la courbe obtenue en soustrayant la courbe (1) de la courbe (2).

On remarque que la réaction Mn^{2+}/Mn est suffisamment réversible pour se prêter à ce genre d'analyse. L'examen de ces courbes nous a permis de fixer le mode opératoire et les conditions de travail. On effectue la préélectrolyse (début t_0) avec agitation de la solution à potentiel constant (v.p. 346) pendant un temps ($t_1 - t_0$) qui dépend de la quantité de manganèse à doser. Puis on arrête l'agitation (temps t_1)

pendant 1 min en maintenant le potentiel constant; on observe une forte diminution du courant (v.p. 351). Puis au temps t_2 on procède au balayage de potentiel de -1.55 à 0 V (v.p. 351) sans agiter la solution. La courbe résultante de cette redissolution ($Mn(Hg) \rightarrow Mn^{2+}$) est représentée à partir de t_2 (Fig. 4). On constate que pendant le balayage et jusqu'au potentiel $E_{eq} = -1.42 \pm 0.01$ V, la réduction domine (Fig. 5). A partir de ce moment l'oxydation l'emporte et devient maximum pour i_m.

Effet de la vitesse de balayage anodique (v) *sur* i_m (Conditions: v.p. 346)

Lorsque v augmente, i_m augmente selon l'expression $i_m = k\, v^{\frac{1}{2}}$ ce qui entraîne une augmentation de la sensibilité de la méthode. Mais la largeur de la vague augmente aussi, ce qui a pour effet de diminuer de façon marquée la sélectivité de la méthode. Si le potentiel d'équilibre reste constant, le potentiel de i_m se déplace vers des valeurs moins négatives. Les courbes de la Fig. 6 résument les résultats de ces essais.

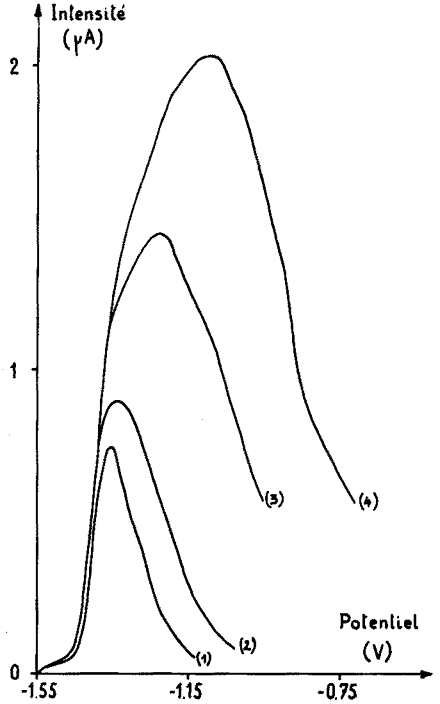

Fig. 6. Courbe de polarisation en fonction de la vitesse de balayage. Vitesse balayage anodique: 1, 0.16 V/min; 2, 0.33 V/min; 3, 1.00 V/min; 4, 2.00 V/min.

Effet de la surface des gouttes sur i_m (Conditions: v.p. 346)

L'augmentation de la surface augmente un peu la sensibilité (v. Tableau V). Quant à la précision elle n'est pas sensiblement modifiée; E_m reste constant. Pour chaque surface nous avons effectué la détermination sur 4 gouttes différentes.

Influence de la durée de préélectrolyse sur i_m (Conditions de travail, v.p. 346)

Nous faisons varier ($t_1 - t_0$) (Fig. 4) en maintenant constant à 1 min le temps de préélectrolyse sans agitation. Les résultats sont donnés dans le Tableau VI. Pour chaque valeur, $t_1 - t_0$, deux essais ont été faits sur deux gouttes différentes. La reproductibilité est bonne. Jusqu'à 6 min, i_m est proportionnel au temps. On peut néanmoins prolonger jusqu'à 15 min la préélectrolyse, le phénomène n'est plus linéaire mais la reproductibilité est satisfaisante. Les abscisses donnent les valeurs de $t_1 - t_0$. On n'a donc pas tenu compte de la minute de préélectrolyse sans agitation, mais dans ces conditions la quantité de manganèse réduite est relativement faible (v.p. 350).

TABLEAU V, INFLUENCE DE LA SURFACE DES GOUTTES SUR i_m

Surface goutte S (mm^2)	*ΔS (%)*	*i_{max} (μA)*	*i_{max} (μA)*	*Δi_{max} (%)*
0.86	3.5	0.650 0.675 0.660 0.670	0.66	±2.1
1.38	2.9	0.785 0.790 0.790 0.805	0.79	±1.6
1.80	2.8	0.905 0.895 0.900 0.895	0.90	±0.7
2.22	3.2	0.970 0.984 0.990 0.985	0.98	±1.2

TABLEAU VI, INFLUENCE DE LA DURÉE DE PRÉÉLECTROLYSE SUR i_m

($t_1 - t_0$) (min)	*1*	*2*	*4*	*6*	*10*	*15*
i_m (*μA*)	0.770	1.450	2.560	3.620	5.620	7.350
	0.785	1.440	2.640	3.620	5.400	7.350

PRÉCISION, SENSIBILITÉ, REPRODUCTIBILITÉ, SÉLECTIVITÉ

Pertes et contaminations

Nous avons établi une courbe d'étalonnage pour des concentrations en Mn^{2+} comprises entre 1 μg/ml et 1 ng/ml ce qui nous a permis de déterminer la sensibilité de la méthode et la reproductibilité. Pour les très faibles teneurs les erreurs sont dues à un grand nombre de facteurs, entre autres aux contaminations, particulièrement celles provenant des réactifs (LiCl, KCl, . . .) et des récipients (par désorption). Nous n'avons malheureusement pas à disposition des laboratoires "propres". Malgré cela nous n'avons pas observé de contaminations par l'air. Il est vrai que le matériel d'analyse est conservé dans de vastes enveloppes de plastique après que celui-ci ait été très rigoureusement lavé par un processus que nous avons mis au point au moyen de traceurs radioactifs. Le lavage s'effectue en deux temps: *lavage acide.* La verrerie est plongée dans une solution chaude de HCl à 10%, puis rincée à l'eau. On procède alors à un *lavage alcalin décontaminant* au moyen d'un bain chaud de RBS 25 à 15%. On rince 3 fois à l'eau distillée et 3 fois à l'eau tridistillée et sèche dans une étuve à 80°, sauf les ballons jaugés qui sont rincés à l'acétone p.a. Merck puis séchés dans une étuve à 50°C. Les pipettes jaugées et graduées ne sont pas lavées à l'acide. On les plonge dans un bain alcalin froid de RBS à 25% puis les rince à l'eau distillée, puis à l'eau tridistillée, à l'alcool, à l'éther et les sèche. Ce traitement est indispensable surtout si les récipients ont préalablement reçu des solutions renfermant du manganèse. Nous avons remarqué qu'un ballon contenant une solution de Mn^{2+} (100 μg/ml), soigneusement lavé, peut encore libérer plusieurs dizaines de ng de Mn^{2+}. En ce qui concerne les pertes, elles sont très faibles dans nos conditions. La présence de l'électrolyte de base diminue considérablement l'adsorption sur les parois; l'atmosphère, si on évite un contact trop prolongé, ne pollue pas les solutions en Mn et le Pb, le Zn ne gênent pas le dosage (v.p. 357).

Courbe d'étalonnage

Elle a été établie pour des concentrations de manganèse comprises entre 1 ng/ml et 0.1 μg/ml avec comme électrolyte de base le KCl Merck suprapur. Pour chaque concentration, 5 dosages complets ont été faits sur des gouttes différentes, mais de même surface.

Pour les autres conditions, v.p. 346.

Les valeurs moyennes de i_m ($\bar{i}_m$) pour chaque concentration, ainsi que les erreurs relatives pour les valeurs moyennes en %, pour $P = 95\%$ sont données dans le Tableau VII. La courbe d'étalonnage est représentée sur la Fig. 7. Nous avons porté en ordonnées les différentes valeurs moyennes de i_m et leur intervalle de confiance correspondant (95%) et en abscisses les concentrations.

La limite de dosage dans ces conditions est de 1 ng/ml.

TABLEAU VII, COURBE D'ÉTALONNAGE

(Mn^{2+}) (ng/ml)	i_m *(μA)*	Δi_m *($\pm$%)*
1.0	0.01156	12.7
5.0	0.03954	3.3
10.0	0.07760	4.0
15.0	0.10690	1.3
20.0	0.14100	4.6
50.0	0.40770	1.9
70.0	0.49260	2.8
100.0	0.76780	3.0

En milieu LiCl p.a. la sensibilité est plus faible et les erreurs sont plus importantes qu'en milieu KCl suprapur .Elles sont dues essentiellement au fait que ce sel renferme des quantités de manganèse très supérieures à celles du KCl suprapur.

Nous avons étudié systématiquement les 3 méthodes de mesure de H_m sur la courbe anodique (Fig. 8). Il en résulte que la méthode des 3 tangentes $H_m{}^1$, de même que celle qui prend comme base la courbe de l'électrolyte de base ($H_m{}^3$) les meilleures. Par contre il est plus facile d'obtenir $H_m{}^1$ que $H_m{}^3$. Dans ce travail, nous avons donc, dans tous les cas, utilisé la méthode des 3 tangentes.

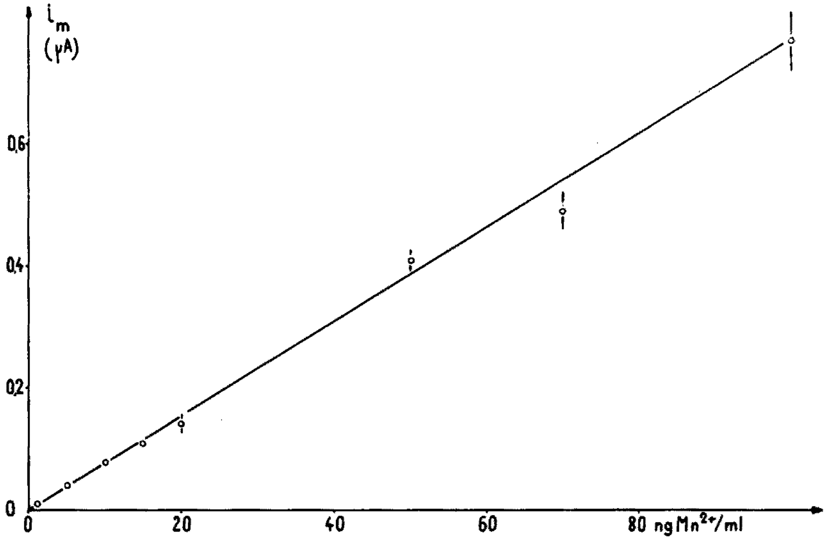

Fig. 7. Courbe d'étalonnage.

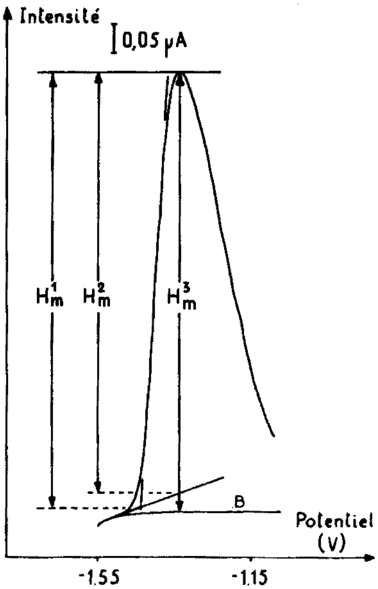

Fig. 8. Détermination graphique de H_m.

Sélectivité

Nous avons vu que d'une facon générale l'effet gênant des particules qui se réduisent à des potentiels voisins de celui du Mn^{2+}, mais qui ne forment pas d'amalgame (composés organiques, H^+, O_2, . . .) est plus marqué en polarographie classique qu'en polarographie inverse car dans ce dernier cas seules les particules dissoutes dans le mercure se réoxydent lors du balayage anodique. Donc les perturbations proviennent surtout de la préélectrolyse. C'est pourquoi O_2 et H^+ ne gênent que s'ils sont en concentration 10 fois supérieure aux ions Mn^{2+}.

D'autre part nous avons examiné l'effet d'un grand nombre d'ions sur le dosage de quantités de Mn^{2+} de l'ordre du ng/ml. Ce sont: Cd^{2+}, Pb^{2+}, Cu^{2+}, Mo^{7+}, V^{5+}, V^{4+}, Al^{3+}, Co^{2+}, Fe^{3+}, Cr^{6+}, Cr^{3+}, Zn^{2+} et Ni^{2+}.

(Conditions de travail: v.p. 346; KCl suprapur; surface de la goutte: 1.38 mm².)

Les résultats sont portés dans la Fig. 9. Les traits pointillés représentent les limites de confiance (95%) déterminées sur des solutions pures renfermant 1 ng/ml d'ion Mn^{2+} ($0.0082\ \mu A < \bar{\imath}_m < 0.0149\ \mu A$) (v.p. 355). Il n'a été fait qu'une détermination pour chaque concentration de chaque ion. Quant à ces dernières elles sont symbolisées par des signes différents. L'examen de la Fig. 9 conduit aux remarques suivantes. Co^{2+} est un ion particulièrement gênant. Il perturbe déjà pour un rapport 1/1. Le Fe^{3+} ne gêne pas, même pour des concentrations de 1000/1 bien qu'au potentiel choisi, une partie de celui-ci précipite. Parmi les éléments gênants à partir du rapport 50/1 citons V^{5+}, Mo^{7+}. Le V^{4+} et le Cr^{6+} ne gênent que pour des rapports supérieurs à 100 et les autres pour des rapports supérieurs à 1000.

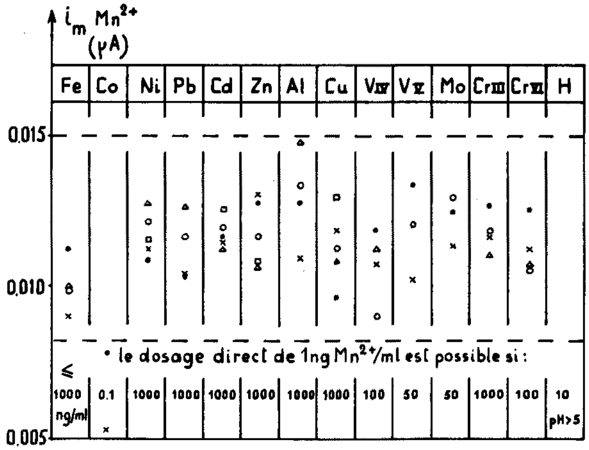

Fig. 9. Sélectivité. ·, 1 ng/ml; ×, 10 ng/ml; ○, 50 ng/ml; △, 100 ng/ml; □, 1000 ng/ml.

APPLICATIONS

Dosage du manganèse dans un produit pharmaceutique: solution de gluconate de manganèse

Cette solution renferme environ 36 µg/ml de manganèse. Ces valeurs sont très élevées pour notre méthode et nous devons avant l'analyse procéder à de très fortes dilutions (6000 à 8000 fois). Pourtant cette opération présente l'avantage de diluer considérablement les substances étrangères, ici le glucose, qui ne gênant plus, nous évite ainsi une séparation toujours délicate dans le dosage de traces.

Mode opératoire. Nous avons eu recours à la méthode par étalon interne. Trois séries (A, B, C) de dosages ont été faites sur 3 échantillons provenant d'un même lot mais de 3 ampoules différentes. Pour chaque solution la polarographie inverse a été effectuée; nous avons procédé comme suit (v. conditions p. 346) en effectuant une polarographie inverse:

(*a*) 25 ml de solution de base (KCl suprapur Merck 0.1 *N*);

(*b*) la même solution (*a*) additionnée d'un volume choisi de solution diluée de gluconate de Mn (25 fois) qui est, pour la série A de 0.080 ml, pour la série B de 0.090 ml et pour la série C de 0.100 ml;

(*c*) la même solution (*b*) additionnée de: série A: 0.050 ml, série B: 0.060 ml, série C: 0.050 ml d'une solution de 1 μg Mn^{2+}/ml;

(*d*) la même solution (*c*) additionnée de: série A: 0.045 ml, série B: 0.045 ml, série C: 0.060 ml d'une solution de 1 μg Mn^{2+}/ml;

(*e*) la même solution (*d*) additionnée de: série A: 0.060 ml, série B: 0.050 ml, série C: 0.060 ml d'une solution de 1 μg Mn^{2+}/ml.

Pour les 3 séries, les valeurs de i_m correspondant à des concentrations connues en Mn^{2+} sont portées sur la Fig. 10. Nous avons ainsi pour chaque série 6 points, soit en tout 24 points, par lesquels nous faisons passer une droite moyenne qui sert de courbe d'étalonnage et sur laquelle on détermine la concentration en portant sur les ordonnées la valeur de i_m obtenue avec les solutions (*b*) (v. Fig. 10 et Tableau VIII).

Nous avons aussi pris séparément les 3 droites correspondant aux séries A, B et C et nous avons reporté sur chacune d'elles la valeur de i_m correspondante sur les ordonnées; les concentrations sont données sur les abscisses.

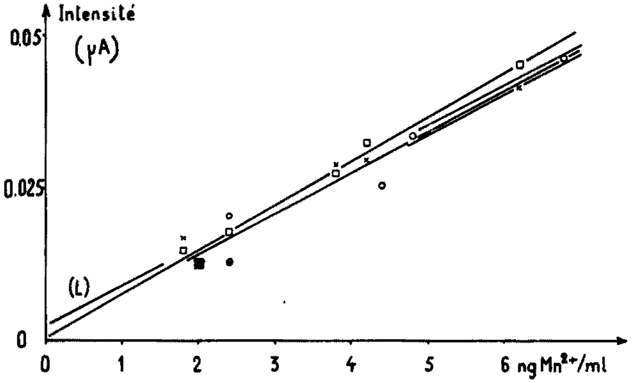

Fig. 10. Dosage de manganèse dans des solutions de gluconate. ×, série A; □, série B; ○, série C.

TABLEAU VIII, DOSAGE DE MANGANÈSE

RÉSULTATS EXPRIMÉS AU MOYEN DE LA DROITE MOYENNE DES SÉRIES A, B ET C

Série	*Teneur en Mn^{2+} des solutions polarogr. (ng/ml)*	*Ampoules (μg/ml)*	*Teneur moyenne des ampoules (μg/ml)*	*Erreur relative max. (en %) par rapport à la moyenne*
A	3.68	28.7	27.8	± 6.1
B	3.76	26.1		
C	4.56	28.7		
A	3.80	29.7	28.2	±10.3
B	3.64	25.3		
C	4.76	29.7		

RÉSUMÉ

Une méthode de dosage du Mn^{2+} par polarographie inverse est proposée. Une étude systématique des divers facteurs intervenant tant au cours de la préélectrolyse que lors de la redissolution anodique, et une étude statistique ont été faites. Un mode opératoire est proposé qui permet de doser 1 ng de Mn^{2+} avec une précision de ±12.7%. Les auteurs ont étudié la sélectivité de la méthode en présence de 14 cations; gênent les ions H^+ si $pH < 5$, le Co^{2+} si sa concentration égale celle de Mn^{2+}, l'oxygène si sa concentration est 10 fois celle du Mn^{2+}; le Mo^{7+} et le V^{5+} gênent lorsqu'ils sont en concentration $\geqslant 50$ fois celle de Mn^{2+}. Les autres ions choisis ne gênent pas à des concentrations 100 et 1000 fois plus élevées. Une application est donnée.

SUMMARY

A method is proposed for the determination of manganese(II) by anodic stripping polarography. A systematic study was made of the various factors affecting the course of pre-electrolysis as well as the anodic stripping. A procedure is given for the determination of 1 ng of manganese with a precision of ±12.7%. The selectivity of the method was studied in the presence of 14 cations; hydrogen ions interfere at $pH < 5$, Co^{2+} interferes at concentrations equal to that of Mn^{2+}, and Mo^{7+} and V^{5+} at concentrations $\geqslant 50$ times that of Mn^{2+}. The other ions studied do not interfere at concentrations 100–1000 times higher. An application to pharmaceutical analysis is described.

ZUSAMMENFASSUNG

Es wird eine Methode zur Bestimmung von Mangan(II) mit der "anodic stripping" Polarographie vorgeschlagen. Verschiedene Faktoren wurden systematisch untersucht, die den Verlauf der Vorelektrolyse und das anodische Auflösen beeinflussen. Es wird ein Verfahren zur Bestimmung von 1 ng Mangan mit einer Reproduzierbarkeit von ±12.7% angegeben. Die Selektivität der Methode wurde in Gegenwart von 14 Kationen untersucht; Wasserstoffionen stören bei einem pH-Wert < 5, Co^{2+} stört bei Konzentrationen, die denen des Mn^{2+} gleich sind, Mo^{7+} und V^{5+} stören bei Konzentrationen, die mehr als das 50-fache des Mn^{2+} betragen. Die übrigen untersuchten Ionen stören nicht bei Konzentrationen, die 100–1000 mal grösser sind. Die Anwendung bei pharmazeutischen Analysen wird beschrieben.

A RAPID METHOD FOR THE DETERMINATION OF ORGANIC NITROGEN AND PHOSPHORUS BASED ON A SINGLE PERCHLORIC ACID DIGESTION

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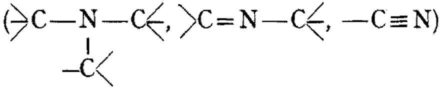
During an investigation on milk lipids in this laboratory, it was found necessary to develop a method for the rapid determination of nitrogen using very small samples of lipid fractions. It is obvious that the lack of such a method is the main reason why most of the published column chromatography, or other fractionation experiments on lipids have been followed almost exclusively by phosphorus estimations.

In the early stages of these investigations a method was devised[1] permitting the determination of amounts of nitrogen of the order of 20–50 μg in (lipid) samples of a very low nitrogen content (0.003 to 0.01%). Since this method was time-consuming (Kjeldahl digestion on a semimicro scale with sulfuric acid, steam distillation in a Parnas–Wagner apparatus, and spectrophotometric measurement of ammonia by nesslerization), it was inconvenient for the analysis of a large number of fractions, and consequently it is useful only for the analysis of samples with very low contents of nitrogen.

In the present paper, a really quick method for the determination of organic nitrogen and phosphorus after a single wet digestion with perchloric acid under reflux (cold finger)is described. This method has proved completely satisfactory for nitrogen analysis of natural products and pure organic compounds, including materials containing tertiary nitrogen of all kinds  $(>\!C{-}\underset{\underset{-C<}{|}}{N}{-}C<,\ >C{=}N{-}C<,\ {-}C{\equiv}N)$. It is especially useful when rapidity of operation is required. This is most important in research on natural products, so that fractionation schemes may be followed. Furthermore, our findings concerning the possibility of using perchloric acid for nitrogen determination should be of general interest, considering the great number of publications on this subject.

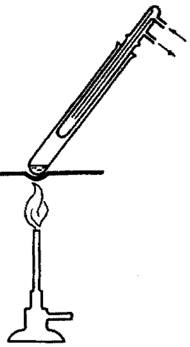
EXPERIMENTAL

Reagents and apparatus

A potassium sulfate–potassium hydroxide mixture for the removal of perchlorate was prepared by mixing 4 volumes of 5 *N* potassium hydroxide with one volume of 6 *N* sulfuric acid. Nessler reagent was prepared as described by LANG[2]. Ammonium molybdate (1.25%) and 1-amino-2-naphthol-4-sulfonic acid (0.064%) reagents were prepared as described by SPERRY[3]. Pyrex tubes 25 × 200 mm and cold fingers of the appropriate size (Fig. 1) were used for the digestion of the samples.

Digestion

Place the sample (containing 5–15 μg of organic nitrogen, and phosphorus in a quantity of the same order of magnitude) in a Pyrex tube and evaporate the solvent if the sample is in solution. Add 0.75 ml of 67–70% perchloric acid and drive the cold finger into the tube (Fig. 1). Start the digestion with very mild heating (at 60–70° for 5 min), continue it at a moderate temperature until the mixture is colorless (or slightly colored), and then boil it vigorously for 5 min after it has completely clarified. In most cases, the whole digestion procedure takes no more than 12–15 min, because the amount of perchloric acid used is much more than the very small amount of organic matter being digested.



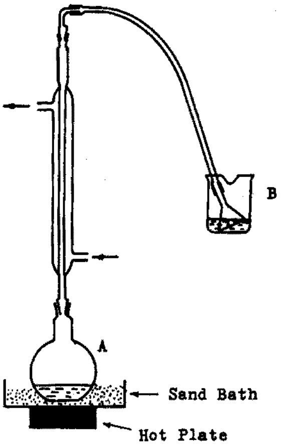


Fig. 1. Pyrex tube with cold finger for perchloric acid digestion.

Fig. 2. Reflux apparatus (see Table II). Beaker B (containing 10 ml of 1 *N* sulfuric acid) was used in order to prevent any loss of ammonia.

After cooling, remove the tube while rinsing the cold finger with distilled water, and adjust the contents of the tube to a volume of 10–12.5 ml. This is effected either with the aid of a mark on the tube at 10, 11, or 12.5 ml, or by rinsing the cold finger with 10 ml of water measured accurately with a pipette.

Nitrogen determination

Transfer 4 ml of the digested sample into another tube and add slowly 1 ml of the potassium sulfate–potassium hydroxide reagent. Transfer 3 ml of the clear supernatant solution into a photometer tube, add 2 ml of water and 1 ml of Nessler reagent, and measure the optical density at 420 mμ, or at 500 mμ for denser solutions[2].

Phosphorus determination

Mix 5 ml of the digested sample with 1 ml of ammonium molybdate reagent, add 0.1 ml (or 2 drops) of the aminonaphtholsulfonic acid solution and heat the mixture in a boiling water bath for 7 min. After cooling, measure the optical density at 830 mμ[4].

Standard curves are prepared by the same methods using samples prepared as follows: 10 ml each of aqueous solutions containing 0, 4, 8, 12, . . . µg of nitrogen and phosphorus (as $(NH_4)_2SO_4$ and Na_2HPO_4) are pipetted into a series of pyrex tubes containing 0.75 ml of the perchloric acid used for the digestion of the samples.

Modification for the milligram range

The procedure described may be modified so that it can be used for any range of nitrogen (and phosphorus) content in the samples under investigation.

In the milligram range the method for nitrogen determination can be simplified as follows. After digesting the sample as described above, dilute it in a volumetric flask, and add Nessler reagent (3 ml) directly to a 5-ml aliquot of the diluted sample (without previous precipitation of the perchlorate). The limits for such modifications are:

Quantity of nitrogen in the sample (mg)	0.1–0.2	0.2–0.5	0.5–1.0	1.0–2.5
Maximum volume (ml) of 67–70% perchloric acid (digestion)	1	2	4	10
Minimum volume (ml) of volumetric flask (dilution)	25	50	100	250

Phosphorus may be determined on a 5-ml aliquot of the diluted sample as described above, after adjusting its pH to 0.7–1.3 by adding 67–70% perchloric acid.

Standard curves must be prepared by the same procedures.

RESULTS AND DISCUSSION

A large number of natural products and pure organic compounds was analyzed by both the present method and the conventional one using sulfuric acid digestion. The results thus obtained (Table I) suggest that the analytical data obtained by the perchloric acid method are equivalent to those obtained by the Kjeldahl sulfuric acid method for all kinds of organic compounds. This is also true for such compounds as hydroxylamine, nitrobenzene, triphenyltetrazolium chloride, azobenzene, and all compounds where nitrogen is bound by covalent bond(s) to atoms of the same or greater electronegativity (*i.e.* N, O, . . .). Such nitrogen was completely lost by both digestion procedures (Table I). Particularly concerning heterocyclic nitrogen strong evidence was obtained that perchloric acid digestion has advantages over the sulfuric acid method. Thus, perchloric acid digestion of nicotinic acid (milligram range) gave reproducible results, being in excellent agreement with the theoretical nitrogen content of the sample, whereas the results obtained by sulfuric acid digestion were 10–15% lower, unless strong heating of the colorless digest was prolonged; by heating the sulfuric acid digest for 1–2 h after it had become colorless, good results were also obtained. The results were similar for caffeine and coffee extracts (comparison of the results obtained by the two digestion procedures).

The method has been used in this laboratory for nearly 4 years, during which time at least 1000 samples have been analyzed in duplicate or triplicate. It has proved highly satisfactory in both the microgram and the milligram range.

Analyses of most of the compounds shown in Table I were repeated using 60–72% perchloric acid. The results were found to be equally satisfactory.

Although the present method does not — at first sight — add much as far as accuracy is concerned, one of its advantages is that under the conditions described the solutions always remain quite clear after nesslerization. Most micromethods based on direct nesslerization after sulfuric acid digestion have a problem at this point, because of the well-known sensitivity of Nessler reagent, and its tendency to form turbid solutions. For the same reason, nitrogen determinations on samples of very low nitrogen content — which are problematic or even impossible by direct nesslerization after sulfuric acid digestion — are possible by the present method.

TABLE I

COMPARISON OF RESULTS OBTAINED BY THE PERCHLORIC ACID PROCEDURE AND THE KJELDAHL SULFURIC ACID METHOD

(The nitrogen contents found by the perchloric acid method are expressed as a percentage of the nitrogen contents determined by the same nesslerization procedure after digestion with sulfuric acid)

Sample	*Nitrogen recovery (%)*
Total lipids of egg yolk	99.5
Polar lipids of milk	98.7
Milk lipid fractions[a]:	
Polyglycerophosphatide plus cerebroside	100.2
Phosphatidylethanolamine	97.9
Phosphatidylserine	99.7
Inositol phosphatides	99.4
Lecithins	100.1
Lecithins plus sphingomyelins	99.7
Sphingomyelins plus mucolipids	98.7
Mucolipids	99.0
Whole milk	99.5
Urine	98.6
Blood serum	99.9
Tea extract	99.8
Meat extract[b]	100.0
Coffee extract[b]	98.4
Corn flour[b]	102.9
Glycine.HCl	99.7
Asparagine.HCl	99.9
Arginine.HCl	98.9
Caffeine	98.3
Nicotinic acid	101.4
8-Quinolinol	100.4
Potassium cyanide	100.9
Azobenzene	In all cases the total amount of nitrogen was lost
Hydroxylamine.HCl	
Triphenyltetrazolium chloride	
Nitrobenzene	

[a] Isolated by silicic acid chromatography as recently described[5]. The main lipid component(s) of each fraction are mentioned in the Table.
[b] Commercial products.

Perchloric acid has been used previously for digestion of organic matter in Kjeldahl nitrogen determination, either alone or mixed with sulfuric acid[6]. It has been also used — but with questionable success — added dropwise during the last stage of the conventional sulfuric acid digestion, as an aid in completing the destruction of organic matter[7–9]. However, many workers in the past have discouraged the general use of perchloric acid for nitrogen determination (for a review on this subject see BRADSTREET[10]), because it is known to be an extremely powerful oxidizing agent and ought to be used with caution, particularly from the standpoint of losses of nitrogen either through formation and subsequent decomposition of ammonium perchlorate or oxidation of ammonium salts to nitrogen.

A detailed study of the action of perchloric acid on ammonia in this laboratory (Table II) showed no indications that either perchloric acid itself, or its thermal decomposition products, had any oxidative effect on ammonia. However, the data given in Table II suggest that ammonia can escape from the digestion mixture even when a reflux condenser is used; but this takes place only in perchloric acid–sulfuric

TABLE II

REFLUX OF AMMONIUM SULFATE WITH PERCHLORIC ACID ALONE, AND WITH A MIXTURE OF PERCHLORIC ACID AND SULFURIC ACID, OR 1 *N* SODIUM HYPOCHLORITE

(Apparatus: Fig. 2; ammonium sulfate (dry), 50 mg; 70% perchloric acid, 5 ml; conc. sulfuric acid, 0–10 ml (see below); reflux on sand bath, 1 h; cooling; quenching of the digest with water; short boiling of both digest and distillate, to remove chlorine[a]. Digest (A): Precipitation of perchlorate by addition of 20 ml of 6 *N* potassium hydroxide; dilution to 1 l; nesslerization. Distillate (B): Dilution to 100 ml; nesslerization)

Experiment no.	*Conc. H_2SO_4 (ml)*	*Elevation of temp.*	*Recovery of nitrogen (% of total)*[b] *Digest*[c] (A)	*Distillate*[d] (B)
1	—[e]	Rapid	99.2	—
2	—[e]	Slow	99.9	—
3	0	Rapid	97.9	0.4
4	0	Rapid	98.8	0.6
5	0	Slow	98.9	0.5
6	0	Slow	100.4	0.1
7	2	Rapid	75.3	24.0
8	2	Rapid	87.4	13.6
9	2	Slow	99.3	1.0
10	2	Slow	99.5	0.2
11	5	Rapid	72.8	27.0
12	5	Rapid	80.0	19.1
13	5	Slow	98.8	2.0
14	5	Slow	100.1	0.0
15	8	Rapid	85.2	14.4
16	8	Rapid	93.7	5.8
17	8	Slow	97.2	1.7
18	8	Slow	98.2	1.9
19	10	Rapid	63.4	36.0
20	10	Rapid	92.1	8.3
21	10	Slow	95.9	3.7
22	10	Slow	98.2	2.0

[a] Excess of chlorine was always found in both flask A ("digest") and beaker B ("distillate").

[b] Considerable or complete loss of ammonia from the digest was observed in all cases when the reflux condenser was omitted, even in the case of perchloric acid alone.

[c] Compared to a standard solution prepared by dissolving 50 mg of ammonium sulfate in *ca.* 200 ml of water and then adding the reagents given above, but omitting heating.

[d] Compared to a standard solution prepared by dissolving 10 mg of ammonium sulfate in 10 ml of 1 *N* sulfuric acid and diluted to 100 ml with water.

[e] Sodium hypochlorite (1 *N*) to the amount of 10 ml added.

acid mixtures where the dehydration of $HClO_4 \cdot 2H_2O$ by sulfuric acid leads to a quick decomposition of ammonium perchlorate and subsequently to a loss of small or large amounts of ammonia, which is mechanically aided to escape by the fumes of perchloric acid and the excess of chlorine produced. The mechanical removal of some of the constituents left in acid mixtures by acid fumes has already been discussed by BETHGE[11]. It is supported by the finding that considerable transfer of ammonia from the "digest" to the "distillate" (Table II) takes place only when the thermal decomposition of perchlorate proceeds rapidly, and even then, it takes place in a non-reproducible manner. The present data and conclusions concerning the action of perchloric acid and chlorine to ammonia are obviously only in rough agreement with the findings of MOORE AND DIEHL[12]. However, any slight differences appearing are eliminated by considering the afore-mentioned non-reproducibility of ammonia losses from unrefluxed perchloric acid solutions, or from perchloric acid–sulfuric acid mixtures even under reflux. The same reason might also explain the discrepancies in analytical results reported by various workers. For instance, MOORE AND DIEHL[12] obtained good results with acetanilide, urea and ammonium sulfate, for which perchloric acid digestion had previously been reported[13] as giving unsatisfactory results.

Consequently, the only question was to ascertain whether destruction of organic matter by perchloric acid proceeds as far as nitrogen is concerned in the same manner as when sulfuric acid is used. The agreement of the analytical data obtained by the 2 digestion procedures (Table I) — even for caffeine, nicotinic acid, cyanide salts and choline which contain representative types of tertiary and quaternary nitrogen — strongly supports it.

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SUMMARY

Results of nitrogen determinations obtained by perchloric acid digestion of organic matter under reflux were found to be equivalent to those obtained by the conventional sulfuric acid Kjeldahl method. A rapid determination of nitrogen and phosphorus was thus possible after a single perchloric acid digestion. Nitrogen was determined by nesslerization and phosphorus by a conventional molybdenum blue technique. The method devised was found satisfactory for a great variety of natural products and pure organic compounds, including materials containing all kinds of tertiary nitrogen.

RÉSUMÉ

Les résultats obtenus pour le dosage de l'azote par digestion à reflux de la substance organique dans l'acide perchlorique, correspondent à ceux de la méthode de Kjeldahl. On peut ainsi doser rapidement l'azote par "nesslerisation" et le phosphore par la méthode conventionnelle au bleu de molybdène. La méthode proposée a donné des résultats satisfaisants pour une grande variété de produits naturels et de composés organiques purs, comprenant des substances avec azote tertiaire.

ZUSAMMENFASSUNG

Bestimmungen des Stickstoffs durch Behandlung organischer Materialien mit Perchlorsäure unter Rückfluss lieferten die gleichen Ergebnisse wie mit der konventionellen Schwefelsäuremethode. Eine schnelle Bestimmung von Stickstoff und Schwefel war so nach einer einfachen Perchlorsäurebehandlung möglich. Stickstoff wurde mit dem Nesslerschen Reagenz und Phosphor nach der Molybdänblaumethode bestimmt. Die Methode ist zufriedenstellend für eine grosse Anzahl natürlicher Produkte und reiner organischer Verbindungen einschliesslich Stoffen, die tertiären Stickstoff enthalten.

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SHORT COMMUNICATIONS

Détermination de l'américium et des terres rares par microanalyse gravimétrique

Les méthodes de détermination quantitative de l'américium se limitent principalement aux techniques spectrophotométriques et aux mesures de la radioactivité de l'isotope utilisé. Un seul dosage pondéral a déjà été signalé: il s'effectue sur le bioxyde AmO_2 obtenu par l'intermédiaire de l'hydroxyde et du nitrate; les différentes manipulations qu'il nécessite en diminuent la précision[1]. Nous avons donc élaboré une méthode de microanalyse gravimétrique de l'américium(III) en réalisant, dans des conditions particulières, la précipitation d'un de ses oxalates. La méthode est généralisable et nous l'avons étendue, en particulier, au dosage gravimétrique des terres rares trivalentes.

Principe

La formation sur papier d'un composé déterminé est utilisée fréquemment en microchimie pour caractériser un élément à l'état de traces et obtenir une estimation de sa concentration[2,3]. Ainsi, la sensibilité des réactions colorées est accrue, car les réactifs agissent sur la totalité de la surface du réseau capillaire du support. Il en résulte une intensification de la coloration[4]. Par ailleurs, si un composé insoluble prend naissance, ses particules sont très fortement retenues dans les mailles de ce réseau et il est possible de les laver sans entraînement appréciable[4]. Cette propriété nous a semblé particulièrement intéressante pour effectuer certaines déterminations gravimétriques à l'échelle microanalytique.

L'originalité de la méthode consiste à réaliser la précipitation sur un support poreux constitué par un papier filtre imprégné d'acide oxalique qui se comporte comme un réactif solide. Ce procédé permet de réduire les pertes et de doser également des solutions diluées (10^{-5} *M*). En effet, dans ces conditions, précipitation et filtration ont lieu simultanément au point d'application.

Conditions opératoires

La condition essentielle est la formation d'un composé insoluble qui soit, d'emblée, ou après calcination, stoechiométriquement bien défini. Le pouvoir absorbant et l'absence de résidu à la calcination nous ont principalement guidés dans le choix du support.

Réaction de précipitation. Les oxalates de l'américium(III) et des éléments trivalents des terres rares précipitent aisément de solutions acides (concentration en ions H^+ de l'ordre de 1 à 2 *N*), par addition d'acide oxalique en excès. Dans ces conditions, l'américium et l'europium forment respectivement les composés cristallins $Am_2(C_2O_4)_3 \cdot 11\ H_2O$ (rose) et $Eu_2(C_2O_4)_3 \cdot 10\ H_2O$ (blanc).

Les études thermogravimétriques faites par MARKIN[5] et WENDLANDT[6] montrent qu'il est difficile d'utiliser ces oxalates pour des déterminations gravimétriques. Par ailleurs, les pesées de précipités sur papier étant peu reproductibles, par suite des variations d'hydratation de ce support, il nous a semblé préférable de les calciner pour obtenir les oxydes AmO_2 (à 470°) et Eu_2O_3 (à 620°).

Préparation du papier réactif. Nous avons choisi le papier Whatman 3MM dont

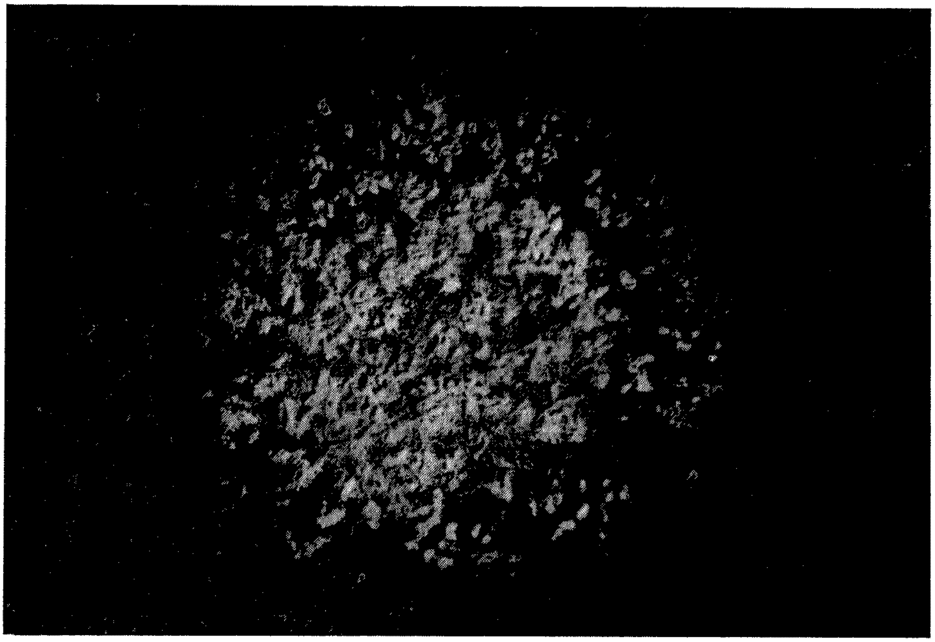

Fig. 1. Précipité d'oxalate d'europium sur papier réactif (grossissement 20).

l'épaisseur et la porosité permettent une absorption convenable de l'acide oxalique et de la solution à doser. En outre, il ne donne pas de résidu appréciable après calcination. L'élimination des traces d'impuretés qu'il renferme éventuellement, s'effectue par lavages successifs à l'aide d'acide nitrique 2 *N*, puis à l'eau. Il est ensuite traité, selon la technique de chromatographie descendante, par une solution aqueuse saturée d'acide oxalique. On obtient ainsi une imprégnation uniforme et reproductible qui correspond à 4.5 mg/cm² de $C_2O_4H_2 \cdot 2\ H_2O$. La conservation de ce papier réactif est excellente.

Mode opératoire. Les dimensions du papier oxalique employé varient évidemment avec le volume de la prise d'essai; ce dernier dépend de l'ordre de grandeur de la concentration de la solution à doser. Nous utilisons couramment des bandes de 15 mm × 90 mm. La solution est déposée au niveau du tiers inférieur de la feuille à l'aide d'une seringue micrométrique "Agla" dont la précision de lecture est $2 \cdot 10^{-4}$ ml. L'oxalate précipite autour du point d'application (voir Fig. 1). La plupart des dosages ont été effectués sur des volumes de 50 à 200 μl. Le précipité, après séchage à l'air, est lavé sur son support par migration d'une solution d'acide oxalique 0.1 *M* selon la technique déjà mentionnée pour la préparation du papier. Une feuille de platine de 6 μ d'épaisseur est calcinée et tarée pour recevoir l'oxalate. Le précipité et son support, ainsi enfermés dans un microcreuset sont portés à température convenable (900°) pour obtenir l'oxyde et une calcination complète du papier. Les pesées sont effectuées sur une balance électromagnétique "CAHN Gram"[7] qui permet des déterminations de 1 μg à 1 g, à 0.01% de l'échelle de mesure choisie.

Résultats et précision de la méthode

Pour vérifier la validité de ce procédé analytique, nous avons comparé les

TABLEAU I

EUROPIUM

Microgravimétrie		*Macrogravimétrie*	
mg/ml	σ^a	*mg/ml*	σ
0.637	0.08	0.672	0.06
1.158	0.16	1.239	0.15
6.195	0.14	6.239	0.15

TABLEAU II

AMÉRICIUM-241

Microgravimétrie		*Gammamétrie*		*Spectrophotométrie*[b]
mg/ml	σ^a	*mg/ml*	σ	*mg/ml*
0.887	0.04	0.860	0.04	0.90
1.286	0.04	1.270	0.01	1.30
1.440	0.06	1.404	0.04	1.46
1.774	0.08	1.812	0.03	1.78

[a] Ecart type = σ.
[b] Les mesures spectrophotométriques ont été effectuées à 815 mμ (ε_M = 64.7; larg. fente = 0.02 mm) en cuves thermostatées à 25°.

résultats qu'il permet d'obtenir aux déterminations que nous avons effectuées par gravimétrie classique, mesure de la radioactivité et spectrophotométrie, après dilutions et prises d'essai convenables (Tableaux I et II).

L'américium-241 ayant été utilisé, les dosages radiométriques furent réalisés par mesure de son rayonnement-γ (énergie maximum = 59 keV).

Les résultats obtenus en faisant les moyennes de séries d'une dizaine de déterminations, sont en bon accord.

Les auteurs remercient Mr. J. P. LARROQUE pour son assistance technique. Ce travail a été effectué dans le cadre de la convention N° 7041/r passée avec le Commissariat à l'Energie Atomique.

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A rapid method for the simultaneous determination of total carbon and carbon-14 in small samples

In tracer experiments with carbon-14 in which milligram amounts of sample are to be analysed, the samples (*e.g.* deposits from engine tests) are often inhomogeneous owing to the presence of small lumps of metals, salts, etc. Since, in general, it is important to know the radioactivity of the samples in relation to their total carbon content, these two variables have to be measured simultaneously on the same sample. Obviously, determinations on different portions of the sample will lead to wrong results. Therefore, we have developed a simple and rapid micro-method involving:

(*a*) combustion of the sample in a quartz tube,

(*b*) absorption of the carbon dioxide in a combined absorption/scintillation liquid,

(*c*) titration of the carbon dioxide,

(*d*) determination of the radioactivity.

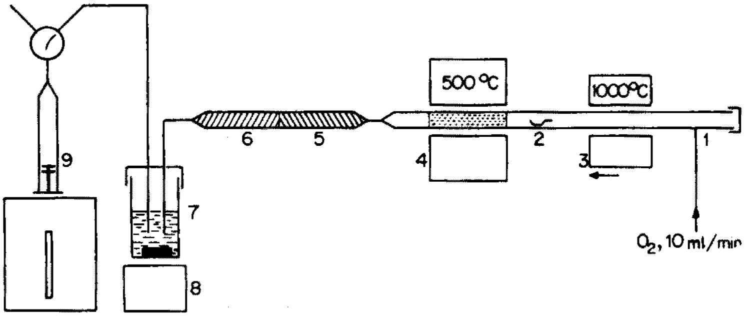

Fig. 1. Combustion and titration apparatus. 1, combustion tube; 2, sample boat; 3, travelling sample heater; 4, Körbl catalyst section; 5, magnesium perchlorate; 6, chromic/sulphuric acid on Sil-O-Cel; 7, absorption and counting vial; 8, magnetic stirrer; 9, piston burette.

TABLE I

COMPOSITION OF ABSORPTION/SCINTILLATION LIQUID

Toluene	900 ml
PPO (2,5-diphenyloxazole)	4 g
POPOP (1,4-bis-[2-(5-phenyloxazolyl)] benzene)	0.2 g
Monoethanolamine	20 ml
Methanol	75 ml
Thymolphthalein indicator	0.2 g

The combustion and titration apparatus is illustrated in Fig. 1. It consists of a quartz tube (1), in which the sample (2) (1–5 mg of material) is burned with the aid of a travelling sample heater (3) in a stream of purified oxygen (approximately 10 ml/min). The combustion gases are passed over an oxidation catalyst at 500° (4) (Körbl catalyst[1]) and next over sections of magnesium perchlorate (5) and of chromic/sulphuric acid on Sil-O-Cel (6)[2] to retain water and nitrogen oxides respectively. The carbon dioxide is absorbed in 10 ml of the absorption/scintillation liquid in a counting vial (7). The composition of this liquid is given in Table I. The carbon dioxide is titrated during the combustion with 0.15 *N* sodium methanolate in methanol, in analogy with a method described by BLOM *et al.*[3]. After the combustion and the titration have been completed (in most cases within a few minutes), the magnetic stirrer is removed and rinsed with 5 ml of methanol. In order to obviate the quenching effect due to the residual colour of the indicator, the solution is decolorized with carbon dioxide, *e.g.* by blowing gently on its surface. Then the vial is closed with its screw cap, thoroughly shaken and placed in a liquid scintillation counter. (We used the Packard Tri-Carb Model 314-X.)

The precision of the carbon determination was approximately 0.5% C (expressed as standard deviation); the precision of the radioactivity depends on the number of counts measured or, in the case of low specific activities, on the sample-to-background count ratio. A counting efficiency of about 40% was found. Because of variations in the final composition of the solutions (due to different amounts of titrant), however, the efficiency of each radioactivity measurement had to be determined by means of an internal carbon-14 standard. No significant effect of dissolved oxygen was found.

Table II gives some results relating to research samples. Some of the duplicate results indeed suggest inhomogeneity. They also show, however, that with the present method this has little or no effect on the specific activity.

TABLE II

DUPLICATE ANALYSES OF RESEARCH SAMPLES

Sample no.	*Intake (mg)*	*Carbon content (% W)*	*Specific activity (disint./min/mg)*
1	2.35; 2.12	66.6; 66.8	32.6; 32.1
2	1.73; 1.74	72.9; 74.1	37.3; 38.7
3	3.98; 3.88	63.8; 59.2	36.3; 36.5
4	5.62; 5.89	80.7; 80.6	35.1; 35.6
5	4.61; 5.44	89.1; 97.8	95.1; 94.8
6	6.69; 4.74	38.2; 41.0	10.2; 10.3

At the moment in this laboratory the new method is used for routine determinations. It permits 20 analyses to be carried out per day. This is a great advantage over the former method, which was based on conversion of the carbon into barium carbonate and required at least 2 h for one determination.

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The determination of gold in cosmic dust collection by nuclear activation analysis

The collection of cosmic dust has interested a number of scientists in recent years. BROWNLOW *et al.*[1] studied the statistics of the distribution and composition of the metallic particles occurring in cosmic dust. However, the analysis of trace elements has not been reported in these iron and nickel fragments.

Since 1962, the joint effort of the University of California, San Diego, California, and the Tata Institute of Basic Research, Bombay, India, has started a year-long continuous collection of the cosmic dust on the offshore islands in the Indian Ocean. Obviously, one cannot expect to collect cosmic dust without much contamination from the ground around the collecting stations, and a magnetic separation treatment has to be applied to the sample in order to remove the large amounts of coral and rocky fragments. The significance of the magnetic separation in cosmic dust collections from various sites has been discussed by PARKIN AND HUNTER[2], PETTERSSON AND FREDRIKSSON[3], and MERRIHUE[4].

In our laboratory, attention has turned to the determination of noble metals in the cosmic dust. Gold, a siderophilic element, which has a high sensitivity for nuclear activation analysis, is expected to be present predominantly in the metal phase together with nickel and iron. It was, therefore, assumed that gold was present in the magnetic fraction of the dust sample. The discussion of cosmogenic significance of the presence of gold in the dust will have to wait for more data of other elements available to us, and only the analytical aspects are hereby described.

The neutron activation technique used for this study was found to be most satisfactory, since it provided the necessary sensitivity and preserved the sample for further investigations. When combined with γ-spectrometry, this method was specific for the analysis of the element under consideration. It was found that the irradiated nuclides always exhibited their proper half-lives, and that the energies of their γ-rays were characteristic. All the common radionuclides which emit γ-rays in the region between 3.5 and 4.8 meV were considered. With the aid of these parameters, a number of common interferences were eliminated, while theoretical calculations of various elements at their cosmic abundance ratio showed that no significant interference would occur during the gold determination as described here.

Dust collection and stripping

A technique similar to that originated by PARKIN AND HUNTER[2] was adopted. A greased petroladum nylon mesh was used, with collecting efficiency of about 50%. The procedure may be described briefly as follows. The nylon mesh was thoroughly washed with detergent solution and then with distilled water. The mesh was exposed at a selected site on an offshore island for about one month. The exposed mesh was then sealed in a clean plastic bag and brought back to the laboratory for chemical and microscopical studies.

The mesh was washed with distilled water to dissolve the salt accumulated from the ocean atmosphere. After it was dried, the mesh was dipped into kerosene and the solution was allowed to settle overnight. The supernatant liquid was decanted off and the residue was transferred to a culture dish. Magnetic particles were attracted to the convex face of a small watch glass attached to the pole of a strong magnet.

This watch glass was carefully removed from the magnetic field and then dipped into a pool of petroleum ether in a larger watch glass placed up above another magnet. All the magnetic particles were thus transferred into the pool and could be examined under a microscope. A separate report will be made on the microscopical findings of the large metallic fragments found in the samples. These large fragments were removed from the magnetic fraction for electron probe analysis, and the neutron activation analysis was performed on the residue which would contain metallic fragments too small for microscopical investigation.

Neutron activation analysis of gold

The individual magnetic samples of the residues from the several collections were treated separately; in turn each one was washed with distilled water, and then dried and placed in a 2-dram polyethylene vial.

The dust samples were irradiated for 30 min together with a gold reference standard, in the rotating rack of a TRIGA reactor in a flux of $1.8 \cdot 10^{12}$ n/cm^2/sec. After irradiation, each sample was placed in a separate, clean, 2-dram polyvial, and accurately weighed. A suitable aliquot of gold standard was pipetted and weighed, and then evaporated to a smaller volume under a hot-lamp to ensure the same counting geometry for both the dust samples and the gold standard.

The samples were allowed to decay for at least 30 h before actual counting of gold in order to circumvent interferences. The γ-ray spectrum of the individual sample was then measured with a 400-channel γ-spectrometer, using a 3×3 in. NaI(Tl) well crystal. The ^{198}Au photopeak, with its maximum at 0.412 meV and a half-life of 2.7 days, was measured by computing the recorded counts from the digital channel readout, after allowing for background radioactivity.

The sample was counted for 900 min daily, and two or three counts were taken. The half-lives of the irradiated products were checked. In all cases the half-lives of the 0.41-meV isotopes were found to be 2.7 ± 0.1 days.

Table I summarizes the results of this study.

TABLE I

AMOUNT OF GOLD FOUND IN VARIOUS SAMPLINGS[a]

	Magn. fraction			*Non-magn. fraction*	
	Weight (mg)	*Count*	*Amount Au (ng)*	*Weight (mg)*	*Count*
Rodrigues (Dec. 26/63–Jan. 28/64)	1.08	$1.4 \cdot 10^4$	0.9	1.64	$1.0 \cdot 10^4$
Kalpeni (Jan. 63)	0.24	$1.5 \cdot 10^4$	1.0	2.34	$7.0 \cdot 10^3$
Minicoy (Nov. 20–Dec. 20/63)	0.17	$7.0 \cdot 10^4$	4.7	—	—
Minicoy (Dec. 20/63–Jan. 20/64)	0.14	$5.0 \cdot 10^4$	3.3	—	—
Kalpeni (Sept. 20–Oct. 20/63)	0.19	$2.5 \cdot 10^4$	1.7	—	—
Rodrigues (Dec. 1–Dec. 24/63)	1.42	$1.8 \cdot 10^4$	1.2	2.28	$3.6 \cdot 10^3$
Kalpeni (Nov. 27–Dec. 27/63)	2.5	$2.0 \cdot 10^4$	1.3	—	—
Rodrigues (Nov. 63)	0.32	$1.0 \cdot 10^4$	0.7	—	—
Ameni-Devi (Dec. 20/63–Jan. 19/64)	0.20	$3.6 \cdot 10^4$	2.4	—	—
Rodrigues (Oct. 1–Oct. 31/63)	1.61	$3.3 \cdot 10^4$	2.2	—	—

[a] Sensitivity of Au gave $1.6 \cdot 10^4$ counts/min/μg, or $1.5 \cdot 10^7$ counts/900 min/μg, or $1.5 \cdot 10^4$ counts/900 min/ng.

It was a surprise that the amount of gold found in various collections was of the same order of magnitude. As a check of the terrestrial contamination accumulated by the meshes, the non-magnetic fraction from a few collections was analyzed in the same manner as mentioned above. It suggests that gold is much richer in the magnetic fraction, and is of extraterrestrial origin. However, its proof is subject to further studies.

The author wishes to express his sincere thanks to Drs. V. P. GUINN and R. A. SCHMIDT of General Atomic/General Dynamics, San Diego, California, who made available their laboratory facilities for part of the neutron activation work. The kind advice of Drs. J. R. ARNOLD and D. W. PARKIN is gratefully acknowledged.

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Determination of manganese(II) in manganese salts of higher oxidation state by electron spin resonance

Electron spin resonance signals can be obtained from certain transition metal ions provided that an odd number of unpaired electrons is present in the ion or complex. With an even number of unpaired electrons no e.s.r. signal is obtained[1]. It occurred to us that electron spin resonance could provide a means for detecting and determining trace amounts of transition metal ions in the presence of a large amount of the same metal in a different oxidation state, *e.g.* Mn(II) in MnF_3 or $KMnO_4$. The determination of Mn(II) in MnF_3 by this method is described here.

Commercially available MnF_3 gave a strong e.s.r. signal at room temperature in the solid state. When dispersed as a solid in potassium chloride a *g*-value of 1.9996 ± 0.0004 was calculated using a stable free radical, diphenylpicrylhydrazyl (*g*-value = 2.0036), as a standard. *g*-Values of 2.000 ± 0.001 have been reported for manganese(II) salts[2] although larger values are also obtained depending on the crystal host[3,4].

An aqueous solution filtered from insoluble MnF_3 gave a strong e.s.r. signal due to manganese(II) recognized by its characteristic 6-line hyperfine spectrum. The known disproportionation of MnF_3 to manganese(II) and manganese dioxide in water did not appear to produce manganese(II) rapidly. Because manganese(II) seems to be the most likely impurity in MnF_3 and since the aqueous solution gave the hyperfine splitting of manganese(II), we conclude the signal in solid MnF_3 is due to manganese(II) as an impurity.

Quantitative measurements of the amount of manganese(II) present in MnF_3 and *g*-value determinations were made by the use of a Varian dual sample cavity of a type first constructed by KOHNLEIN AND MÜLLER[5]. The method used is essentially as suggested by the Varian Associates instrument division. A known amount of $MnSO_4 \cdot H_2O$ was used as a standard. The signal from the known and unknown samples in the dual cavity is modulated at 100 kc and 400 c.p.s. and recorded on a dual-channel recorder. The first moment of each of the signals is obtained and the sample positions reversed. The first moment is calculated for the reversed position. From an expression involving only the values of the moments and the spectrometer gain settings the ratio of the known to the unknown amount of manganese(II) can be obtained:

$$\frac{N_{\mathrm{k}}}{N_{\mathrm{u}}} = \left[\frac{M_{\mathrm{k}_1} G_{\mathrm{u}_2} M_{\mathrm{k}_2} G_{\mathrm{u}_1}}{M_{\mathrm{u}_2} G_{\mathrm{k}_1} M_{\mathrm{u}_2} G_{\mathrm{k}_2}}\right]^{\frac{1}{2}}$$

where N = number of spins, M_1 = first moment before reversing samples, G_2 = spectrometer gain settings after reversing samples, k = known, u = unknown. If $f'(w)$ is the resonance, $\int_{-\infty}^{\infty} f'(w) w \, dw = M$. From this calculation MnF_3 was found to contain 0.3% of manganese(II).

Application can be made to the quantitative estimations of manganese(II) in salts of permanganate, manganate or manganese dioxide or in four-coordinated manganese(II) complexes such as manganese(II) acetylacetonate[6] since these hosts themselves do not give electron spin resonance signals. With suitable integrating devices such determinations could be performed rapidly and routinely.

MnF_3 was obtained from K and K laboratories. This work was supported by funds provided through the Director of General Research of the University of Georgia.

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(Received August 23rd, 1965)

BOOK REVIEWS

J. KRUGERS AND A. I. M. KEULEMANS, *Practical Instrumental Analysis*, Elsevier Publishing Co., Amsterdam, 1965, ix+263 pp., price Hfl. 30.00, 60 s.

It would be denied by none that there has been a rapid development and extensive application of instruments to analytical problems in recent years. Further, there is little doubt now, even among classical analysts, that this has been to the benefit of all. As instrumental techniques develop, however, the necessity of having suitable and reliable textbooks increases, perhaps even more than in any other branch of analytical chemistry. At present, few such books are available and are in the main from American sources. It is, therefore, with interest that the present volume from the Dutch school is received.

In any volume dealing with instrumental analysis, there are several aspects of the treatment that can make the book a success or merely a volume for occasional reference. The more important of these might be enumerated as (*1*) a suitable and satisfactory selection of techniques, (*2*) a sound and extensive description of the principles involved, (*3*) attention to the commercial instruments available and (*4*) the types of application of the technique.

On the first of these requirements the present volume comes out very well. A wide range of modern, useful techniques is presented, including absorption photometry (ultraviolet, visible and infrared), spectropolarimetry, flame photometry, emission spectrography, X-ray fluorescence analysis, chromatography (adsorption, gas, thin-layer), activation analysis, polarography, coulometry, electrophoresis, differential thermal analysis, NMR, and mass spectrometry. A modern technique, of which only brief mention is made, in the chapter on ultraviolet–visible spectrophotometry, is atomic absorption spectrophotometry. This might have merited a chapter in its own right. Fuller treatment of attenuated total reflectance would also have been valuable.

Each chapter has been written by a different author or authors, who have had considerable experience in operating the techniques about which they write. In general, each chapter dealing with a particular technique gives an outline of the principles, the instrument or instrumental arrangement, applications, and in some cases future developments. Because of the different authors, chapters vary considerably, but several common features should be mentioned. Principles are discussed quite briefly, without an attempt to go into great detail, and only general applications are usually discussed.

The book will be of interest and value to various shades of industrial chemists, who will find the chapter on the application of instrumental methods in Process Analysis to their liking. The chapter on applications in clinical chemical laboratories will interest biochemists and those who work in hospital laboratories. The value to students at the undergraduate level is more difficult to assess. Usually, a book aimed at this level requires extensive treatment of theory and many examples of application; the examples of typical uses with analytical instructions given in the appendix to the book, go some of the way to meeting this latter requirement.

R. J. MAGEE (Belfast)

J. KUCHARSKÝ AND L. ŠAFAŘÍK, *Titrations in Non-aqueous Solvents*, Translated by K. ŠUMBERA, Elsevier Publishing Company, Amsterdam, 1965, xii+286 pp., price 70 s.

This monograph consists of two interlinked sections. The first (115 pp.) serves to give the reader a firm, but not too mathematical, background to non-aqueous titrimetry. It includes discussions on acid–base theories, solvents (including their purification), titrants and primary standards. The chapter on end-point indication deals not only with visual methods but also with potentiometric, coulometric, conductimetric (and high-frequency) and photometric titrations.

The practical aspects are dealt with in the second section. After a description of the "methodology" of the titrations, methods are given for the determination of a host of compounds, most of them organic. The compounds are discussed in groups, *e.g.* amino acids, vitamins, etc., and extensive practical details are preceded by a literature survey. Non-aqueous redox titrations and equivalent weight determinations, and a useful tabulation of the physical properties of 40 solvents are included in this section.

The book, which is the second revised edition of one that originally appeared only in the Czech language, is superbly produced. The subject matter is well and accurately presented, and a good balance between theory and practice is achieved. The almost faultless translation adds the final veneer to a very commendable publication. It is an essential text for all analytical chemists who are concerned with non-aqueous titrimetry, and it will do much to convince the sceptics of the remarkable versatility of this technique.

ALAN TOWNSHEND (Birmingham)

D. D. PERRIN, *Organic Complexing Reagents: Structure, Behavior and Application to Inorganic Analysis*, Chemical Analysis Series, Vol. 18, Interscience Publishers–John Wiley & Sons, Inc., New York–London–Sydney, 1965, xi + 365 pp., price 90 s.

The book begins with a concise, yet comprehensive, review of modern inorganic chemistry. This is developed into an explanation of the theory underlying the use of a host of organic reagents in analytical chemistry, not only for cations but also for anions and neutral inorganic molecules. The main treatment deals with reactions from the standpoint of the ligands, but there is also a chapter on the reactions of the individual elements.

Although there are many points that are disputable, as is unavoidable when definite scientific evidence is lacking, the overall interpretation is excellent. The generous sprinkling of structural formulae is a particularly praiseworthy feature of this very welcome, and indeed much-needed book.

A. TOWNSHEND (Birmingham)

D. Hummel, *Identification and Analysis of Surface-Active Agents by Infrared and Chemical Methods*, Translated by E. M. Wulkow, Interscience Publishers-J. Wiley Inc., New York, 1964, Text Vol. xiv+386 pp., Spectra Vol. 156 pp., price 150 s.

An ever-growing number of surface-active materials of varied chemical constitution is being used in industry and in the home. Their use has solved many problems but has also created new ones: drinking water pollution, survival of river fauna, biodegradability. Therefore the present monograph, which covers the identification, analysis and infrared spectra of surface-active compounds, should be of interest to a wide range of specialists.

The text volume starts with a brief survey of the chemistry of surfactants, followed by a "Letter-Number" classification based on electrochemical behaviour and functional groups. The next 5 chapters discuss the analytical methods: electrochemical behaviour, infrared spectroscopy, chemical methods of functional group analysis, separation from non-surfactants and finally methods of quantitative analysis. The volume closes with 20 detailed tables, giving the composition of more than 250 commercial surfactants and methods for their detection and classification. The spectra volume presents 466 infrared spectra of anionic, cationic, nonionic and amphoteric surface-active compounds. Eight charts show the intensities of absorption bands classified according to functional groups present in the molecule.

The most important contribution of the monograph is undoubtedly the collection of infrared spectra—the first to appear in book form—and the chapter dealing with the infrared spectroscopy of surfactants. The chapters on chemical analysis and separation techniques are rather brief and should be considered as an introduction to the field.

The book is a translation of the German edition which appeared in 1962 under the title "*Analyse der Tenside*". The introduction of the term "tenside" might be justified in German to replace "grenzflächenaktive Substanz" but not necessarily in English, in view of the well established terms available. The monograph as a whole will be a valuable addition to the library of anyone concerned with surface-active agents.

F. C. A. Killer (Oxford)

Anal. Chim. Acta, 34 (1966) 378

Methods of Biochemical Analysis, Edited by D. Glick, Vol. 12, Interscience, New York, 1964, ix+499 pp., price 113 s.

As in previous volumes in this series, the reviews fall into two categories. Two deal with techniques of wide applicability, while five are concerned with individual compounds or with groups of compounds.

In the first category Natelson and Whitford consider the determination of elements by X-ray emission spectrometry. A detailed account is given of the instrumentation of the technique and procedures are described for its application to biological materials, *e.g.* blood serum, without processing or after processing by ashing, solvent extraction, vaporisation, precipitation, compression or plating. The methods described are applicable to any type of instrument.

In the second general article MANGOLD, SCHMIDT AND STAHL give an account of thin-layer chromatography, a relatively new technique which is rapidly becoming indispensable to biochemists. Methods for the preparation of plates, application of samples, development, visualisation and quantitation are described and the versatility of this important technique is illustrated in sections dealing with preparative, adsorption, ion-exchange, partition and reversed-phase thin-layer chromatography and with the use of polyamide and dextran gels.

YALOW AND BERSON contribute a specialized article on the immuno-assay of plasma insulin using the ^{131}I-labelled hormone. The method depends on the competitive inhibition of the formation of an antigen–antibody complex of labelled insulin and specific antibody. The preparation of anti-serum and of ^{131}I-insulin is described and a protocol given for the assay. The behaviour of labelled insulin in paper chromatography and electrophoresis is also considered.

SJÖVALL discusses the separation and determination of bile acids. Separations by all types of adsorption and partition chromatography and by counter-current distribution are considered and the application of methods of estimation directly and to the acids after chromatographic separation described. In a final section the application of the procedures described to bile and small intestinal contents, blood and faeces is discussed.

Workers in the field of thyroid biochemistry are served well by an article by ROCHE, MICHEL AND LISSITZKY on the analysis of natural radioactive iodine compounds by chromatographic and electrophoretic methods. This may be regarded as a supplement to the authors' review in the first volume of this series. The chief sections deal with the synthesis of labelled thyroid hormones, their separation by zone and column electrophoresis, the paper chromatography of iodoamino acids and their derivatives and column chromatography of natural iodinated compounds.

The remaining two articles are the longest in the present volume. In the first, STORVICK, BENSON, EDWARDS AND WOODRING review chemical, physical and enzymic methods of determining vitamin B_6 and methods of separation are described. Full experimental details are given of the methods discussed. COTLOVE deals with the wide variety of methods which have been applied to the estimation of chloride in biological materials and makes an authoritative evaluation of their applicability to a wide range of biological problems. Particular attention is paid to electrometric and isotope dilution methods which have been developed recently and have resolved a number of long-standing analytical difficulties.

Once again biochemists are indebted to the authors and editor of this series, the high standard of which is maintained by this twelfth volume. It should be included in all collections of books available to those engaged in biochemical research.

H. G. BRAY (Birmingham)

Anal. Chim. Acta, 34 (1966) 378–379

ANNOUNCEMENTS

SYMPOSIUM ON PYROLYSIS – GAS CHROMATOGRAPHY, PARIS – SEPTEMBER, 1966.

A symposium on Pyrolysis–Gas Chromatography will be held at the Ecole Polytechnique, 17, rue Descartes, F 75 – Paris 5, on September 15–16, 1966.

It will deal with the use of pyrolysis–gas chromatography in the analysis of non-volatile organic compounds, mainly high polymers, but also biological samples, compounds of biological interest and more simple organic molecules. The use of pyrolysis-chromatography as an identification tool and in kinetic studies will also be discussed.

Contributed papers are invited in all aspects of pyrolysis-chromatography. An abstract (not more than 500 words) must be submitted before June 15. Financial assistance for travel will be available to authors of papers accepted from abroad.

Abstracts of papers, inquiries concerning the symposium and registration should be directed to: Dr. G. GUIOCHON, Ecole Polytechnique, 17, rue Descartes, F 75, Paris 5.

SYMPOSIUM ON PHYSICAL SEPARATION METHODS IN CHEMICAL ANALYSIS, AMSTERDAM – APRIL, 1967

The Analytical Chemistry Section of the Koninklijke Nederlandse Chemische Vereniging is organizing an international symposium on "Physical Separation Methods in Chemical Analysis". It will be held in Amsterdam on 10–14 April 1967, and will cover, among other things:

Chromatography, distillation, multi-stage partition, zone melting, fractional crystallization; thermodiffusion, dialysis; ultracentrifugation; electrophoresis, and electrodialysis.

The mornings will be devoted to papers by specially invited contributors and the afternoons to papers submitted for discussion. Preprints will be sent to all participants and the papers, together with the discussions, will be published after the symposium. Excursions to various industries in the area and sightseeing trips are also planned.

Details regarding the titles of the invited papers, names of the main contributors and submission of the afternoon papers will be announced later. Further information can be obtained from Dr. C. L. DE LIGNY (Secretary), Analytical Chemistry Laboratory, Rijksuniversiteit, Utrecht, The Netherlands.

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The University of Birmingham, Great Britain

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Research Department, Imperial Chemical Industries Ltd.,
Manchester, Great Britain

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Second International Symposium organized by the Chromatography
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