

ON THE CONCENTRATION AND SEPARATION OF THE TRACE ELEMENTS: Fe, Cu, Zn, Mn, Pb, Mo and Co*

I. ION EXCHANGE METHODS

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GENERAL INTRODUCTION

Owing to the increasing demand for rapid results in analytical chemistry, there is a general trend to automation, but at the same time the problems posed become more and more complex. It is thus impossible to do without classical chemical methods and separation techniques, such as ion exchange, solvent extraction and paper chromatography (*cf.* WHITE¹). This statement is certainly true for trace analysis, where automation is only possible to a very small extent. Only in a limited number of cases (for instance, in some activation methods and in X-ray-fluorescence) is the determination of micro constituents feasible without any classical chemical treatment. Generally, some pretreatment is inevitable, and usually involves concentration of the traces, separation from the macro-constituents and mutual separations. In fact, the development of the separation techniques mentioned above has been greatly stimulated by the importance of trace analysis.

A satisfactory pretreatment should (1) concentrate the trace elements to a level at which they can be determined with the accuracy required, (2) separate the ions to be analysed from interfering constituents and (3) not introduce any compound interfering with the subsequent quantitative determination(s). In some radiochemical separations, a rapid method is required, owing to the short half-lives of the nuclides concerned.

This study is restricted to ion exchange (part I), solvent extraction (part II) and paper chromatography (part III), the results being compared at the end of part III. Elegant solutions of the problem are of course also offered by other methods, but none of these techniques has been so generally accepted as the three mentioned above (*cf.* NORRIS²; COOKE³). Precipitation must be rejected because of the adsorption-, occlusion- and coprecipitation-effects involved.

A further restriction is made to the ions of iron(III), copper(II), zinc(II), manganese(II), lead(II), molybdate and cobalt(II), while sodium, potassium, calcium, magnesium, phosphate and sulfate ions are considered to be macro-constituents (this classification refers to the situation in the animal field. Application of our results to other fields is of course possible in many cases).

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Separations are primarily considered in connection with radiometric determinations of the trace elements, but they are also applicable to other quantitative techniques.

INTRODUCTION TO ION EXCHANGE STUDY

Many new techniques have been developed since RICHES⁴ and LUR'E AND FILIPPOVA⁵ carried out their experiments on the concentration of trace elements by ion exchange. Apart from more efficient concentration techniques, separations of many inorganic ions have been developed. Reviews have been given by ABRAHAMCZIK⁶, KRAUS⁷, KUNIN^{8,9} and HUDGENS¹⁰.

Three different approaches to the problem can be distinguished*:

(1) *Specific ion exchange materials* were developed as a parallel to the natural occurring specific metal-complexes. SPECKER *et al.*^{11,12} separated iron(III) from other cations and also separated Cu, Zn, Mn, Pb, Co, Ca and Mg from alkali metals; CORNAZ AND DEUEL¹³ devised a selective method for iron(III); BAYER¹⁴ obtained a separation of copper and cobalt from zinc, magnesium and barium; KULČICKÝ¹⁵ prepared a selective exchange material for copper. GRIESSBACH¹⁶, TROSTYANSKAYA AND TEVLINA¹⁷ and KUNIN¹⁸ have reviewed the field.

Future developments will be of considerable interest but a solution to our problem on this basis seemed to be rather improbable.

(2) *Specific complexing agents*, added either to the sample solution, to the eluant, or to the column itself, have been used by many authors and remarkable results have been obtained, *e.g.* in the separation of the rare earth elements. Unfortunately, many complexes interfere with (most of) the subsequent quantitative determinations and thus one of the major advantages of ion exchange is lost. The negatively charged chloro-, bromo-, and fluoro-complexes do not suffer from this disadvantage. A separation of many metals by anion-exchange of their chloro-complexes is possible, as was shown by MOORE AND KRAUS¹⁹. A review of the extensive literature with Dowex I X 10 has been given by KRAUS AND NELSON²⁰ while results with Wofatit-150 have been reviewed by JENTZSCH²¹. Alcohol-hydrochloric acid mixtures were used by WILKINS *et al.*²² and by BERG AND TRÜMPER²³. Unfortunately, with the ashes of biological samples, precipitates of the major constituents are obtained in concentrated solutions of chloride or bromide, thus this method can only be used when the major constituents have been previously removed.

(3) *Specific elution of cation-exchange columns with organic solvents* has been practised by only a few authors: KEMBER *et al.*²⁴ separated copper from iron and nickel on Zeocarb 225-H with mixtures of acetone, hydrochloric acid and water. Later these authors²⁵ recommended Amberlite IR-112. IONESCU *et al.*²⁶ and BUZNEA *et al.*²⁷ separated copper and zinc with a similar solvent on the ion-exchange materials KU-2 and R-21.

As this method does not suffer from the disadvantage mentioned above, it was chosen for our experiments. Radioactive tracers were used to facilitate the evaluation of the results.

EXPERIMENTAL

Materials

Choice of the resin. Many resins collapsed in the elution mixtures. Amberlite IR-112

* Other ion exchange procedures, *e.g.* electro ion exchange are not considered here.

and Amberlite XE-100 (which according to the manufacturer, Rohm and Haas, Philadelphia (U.S.A.), have the same properties) were the most satisfactory.

Chemicals (not radioactive). Ion exchange water was used, which had a resistivity of at least 3 Megohms. The sulfuric, perchloric, hydrochloric and nitric acids and the ammonia were of "AnalaR" quality and had specific gravities of 1.84, 1.54, 1.18, 1.42 and 0.88 respectively. Nitrates and chlorides were used for the inorganic salts; all reagents, including: sodium pyrophosphate, disodium phosphate, hydrogen peroxide (30%), potassium iodide, hydrazine hydrate, methanol, ethanol, chloroform, acetone (containing 1% water), rubenic acid and titan yellow, were of reagent grade (either AnalaR or Merck *p.a.*).

Radio-active chemicals. Dilutions from a small volume to 1 ml are given and (between brackets) the amounts of the anion or metal used per experiment (in ml, μC and μg respectively; for molybdenum, which has a short half life, a medium value for the amount in μg is given).

$^{35}\text{SO}_4^{-2}$: 66 μC $\text{Na}_2^{35}\text{SO}_4$ (carrier free) in water, diluted with 0.01 *M* sulfuric acid to 1 ml (0.001-66-0.5).

$^{32}\text{PO}_4^{-3}$: 17 μC $\text{Na}_2\text{H}^{32}\text{PO}_4$ (carrier free) in water, diluted with 0.01 *N* phosphoric acid to 1 ml (0.001-17-0.33).

^{59}Fe : 150 μC $^{59}\text{Fe}^{+3}$ (33 μg) in 1 *N* hydrochloric acid, diluted with the same acid to 1 ml (0.001-160-0.05).

^{65}Zn : 200 μC $^{65}\text{Zn}^{+2}$ (1000 μg) in 1 *N* hydrochloric acid, diluted with the same acid to 1 ml (0.001-200-1).

^{210}Pb : 100 μC $^{210}\text{PbCl}_2$ (Radium-D in equilibrium with its decay products) in 2.5 *N* nitric acid, diluted with 9 *N* hydrochloric acid to 7 ml; 210 μg of inactive lead was added, the decay products were removed by anion-exchange through a 5-ml column of Dowex 1 X 10, and the eluate was diluted with 9 *N* hydrochloric acid to 10 ml (0.1-1000-0.22)*.

^{99}Mo : 30 μC $(\text{NH}_4)_2^{99}\text{MoO}_4$ (2500 μg Mo) in water, diluted with water to 1 ml (0.005-150-12.5).

^{54}Mn : 10 μC $^{54}\text{MnCl}_2$ (carrier free) in 0.1 *N* hydrochloric acid, diluted with 1 *N* hydrochloric acid to 1 ml (0.01-100-10⁻⁵).

^{60}Co : 100 μC $^{60}\text{Co}^{+2}$ (10 μg) in 1 *N* nitric acid, diluted with this acid to 1 ml (0.001-100-0.01).

^{89}Sr : 1.25 μC $^{89}\text{SrCl}_2$ (carrier free) in 0.1 *N* hydrochloric acid, diluted with *N* hydrochloric acid and 10 mg of Sr as SrCl_2 added (0.001-800-10).

^{45}Ca : 0.25 μC $^{45}\text{Ca}^{+2}$ (0.2 μg) in 0.1 *N* hydrochloric acid, diluted with 1 *N* hydrochloric acid (0.1-26-0.02).

Apparatus

The column consisted of a pyrex glass tube (Fig. 1), fitted with a removable funnel (A) and a fused-in filterplate (B).

Measurement of radio-activity was performed with an end-window GM-tube (Philips 18506), a GM-tube for liquid samples (20th Century Electronics M-6) or a well-type NaI-crystal (Philips PW 4111/W), all combined with a scaler (Philips 4022-32-52). With the crystal sometimes a single-channel analyzer was applied (E.K.A.F. 30301-20102).

* For details see ref. 28

Further apparatus: Beckmann-DU spectrophotometer with flame attachment; Photovolt densitometer with scanning attachment; Beckmann-G pH-meter.

Wet ashings were performed with the apparatus shown in Fig. 2. The pyrex glass tubes (A) were cleaned with sulfuric-chromic acid and then with 3% hydrofluoric acid and were kept under 2 *N* nitric acid. These tubes were heated on the aluminium case (B) over an infrared heater (C), fitted with a mirror (D). Reagents were added through (E) and vapors removed through (F).

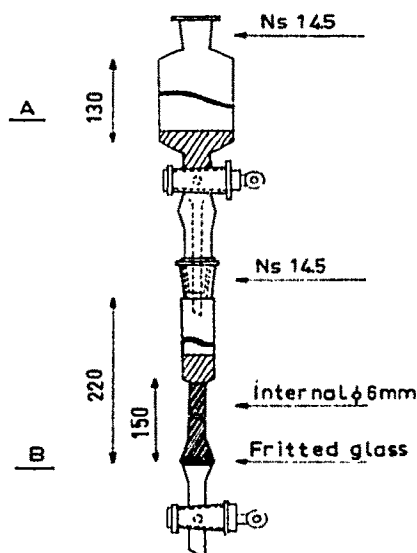


Fig. 1. Ion exchange column.

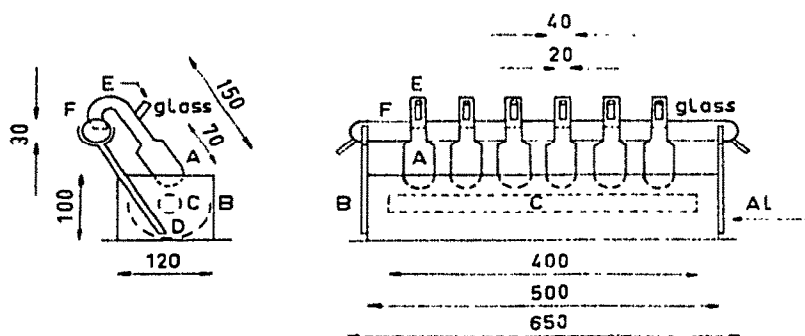


Fig. 2. Ashing apparatus.

Pretreatment of the ion-exchange column and the sample

The ion-exchange material was treated with 0.5 *N* hydrochloric acid and added to the column as a slurry. After a final wash with 10 ml of the 0.5 *N* and acid 10 ml of water, it was ready for use.

The length of the column depended on the amount of cations to be analysed. As the capacity of the wet resin is about 2 milliequivalents per ml and the column can be

loaded with cations to about 20% of its capacity, a column of 15 cm (4 ml) is sufficient for 1.6 milliequivalents of cations (or for the ash of 3 g of dry cow liver or 0.8 g of dry grass for instance).

About 1 g of the air-dried sample was ashed with 0.5 ml of sulfuric acid and some nitric acid. Either hydrogen peroxide or perchloric acid was used to clarify the solution. The latter reagent was only added when the mixture contained no coarse particles. After cooling, the solution was diluted with water to 100 ml and added to funnel A of Fig. 1.

Separation technique

The solution of the ash in general had a pH between 1 and 2. Although this value is rather low for sorption by cation-exchange material, it was not increased owing to possible losses of iron(III) at higher pH values. SAMUELSON²⁹ reported such losses and ascribed them to the formation of colloidal hydroxide*.

Our own experiments, carried out with the ash of 1 g of dry cow liver containing about 300 μg of iron(III) in 100 ml, denoted a loss of: 0, 0.5, 10 and 25% at pH 2.0–2.5, 3.0 and 3.5 respectively.

Sorption was carried out slowly (a flow rate of 10 ml/min/cm²) in order to obtain homogeneous loading of the column and sharp separations. The last traces of the anions were washed out with 0.01 *N* hydrochloric acid in order to keep the iron(III) adsorbed on the column.

Before the separation (with the acetone–hydrochloric acid mixtures) the column had to be adjusted to the right acetone concentration with a mixture of acetone and water. Gas bubbles were formed during this treatment (by evaporation of the acetone) but their influence on the efficiency of the separation proved to be small. A cold-water jacket can be used to minimize this effect.

Mixtures of several of the lower esters, alcohols and ketones with aqueous solutions of hydrohalic acids were investigated for the *selective elution*. Acetone–hydrochloric acid was found to be the most satisfactory. Separation into the groups, Fe, Cu, Zn, Pb — Co, Mn — Na, K, Ca, Mg was achieved with acetone–hydrochloric acid mixtures of different composition. The separation of copper and cobalt was the most difficult; separation was obtained more rapidly with a solvent containing acetone–hydrochloric acid–0.01 *N* potassium iodide (89:1:10) to which some hydrazine was added to prevent oxidation. The excess of iodide interfered with most subsequent quantitative determinations, hence it had to be oxidised and the iodine boiled out, which made the method more complicated.

With 15-cm columns, 100 ml of acetone–hydrochloric acid was required for each elution; a velocity of 3 to 4 ml/min/cm² had to be maintained to achieve sharp separations.

The eluates were collected in "Teflon" dishes and before analysis the acetone was evaporated in a clean atmosphere. The columns were regenerated with 2 *N* hydrochloric acid, which eluted Na, K, Ca, Sr, Ba and Mg, and were finally washed with water.

* The difficulties encountered by HAMM³⁰ in the sorption of iron(III) were due to the formation of excessive amounts of pyrophosphate in his dry-ashing technique. In wet-ashing only traces of this anion are formed.

Analytical methods

The efficiency of the separation was tested:

(1) *With radio-isotopes* (see *Materials*, p. 44). ^{45}Ca and ^{35}S were measured with the end-window GM-tube, ^{89}Sr and ^{32}P with the M6 GM-tube and the other isotopes with the scintillation counter. With the aid of the single channel analyser several isotopes could be measured simultaneously. All measurements were performed in solution, except for the fractions containing ^{45}Ca or ^{35}S which had to be evaporated in an aluminium dish.

(2) *Magnesium* was determined with titan yellow following SANDELL³¹. For *copper* a densitometric method with rubeanic acid was preferred as it allowed the measurement of a large number of samples (parts of the eluates) in one procedure*.

Strips of Whatman No. 1 paper (2.5 \times 50 cm) were washed** chromatographically in the descending way with (a) 9 : 1 methanol-hydrochloric acid, (b) 9 : 1 methanol-ammonia and (c) 95 : 5 methanol-water, each washing lasting 24 h. The washed paper had a copper-content of less than 0.01 $\mu\text{g}/\text{cm}^2$ as was determined by ashing two strips and applying the determination described below.

With a micropipet 0.01 ml of the eluate of the ion-exchange column (or its concentrate***) was placed on a washed paper strip, dried for 2 h, neutralized by placing for 1 h in ammonia vapor and sprayed with a 0.5% solution of rubeanic acid in ethanol on both sides. The spray was of an ordinary type, the current of air being delivered automatically in order to obtain a steady stream of the reagent. The paper strip was moved by hand, but as continuously as possible, before the sprayer at a distance of about 20 cm. This spray was repeated 2 or 3 times. The dried spots were measured with the Photovolt densitometer, a slit of 0.1 \times 0.6 cm and a color filter with a maximum at 630 m μ being used. Beer's law was followed from 0.1 to 2.0 μg of copper/0.01 ml.

When standards were placed between the samples the standard deviation was 8% and 4% for the ranges of 0.1-1.0 and 1.0-2.0 μg of copper respectively. Microgram amounts of cobalt and nickel interfered; a reagent-blank had to be subtracted.

(3) Finally, *sodium and potassium* were analysed by flame photometry, with which less than 0.004 and 0.2 μg per ml of the respective elements could be determined.

RESULTS

The figures given in Tables I, II and III were all found as a mean of 4 experiments with the ash of 1 g of dry cow liver. Table I shows the separation of cobalt from Cu, Fe, Zn and Pb (manganese behaves similarly to cobalt). It is clear that the mixture 93-1-6 is to be preferred (the acetone contained an additional 1% of water).

Table II shows the separation of cobalt and manganese from calcium (the other

* A similar method using either 8-hydroxyquinoline or 7-iodo-8-quinolinol-5-sulfonic acid proved to be suitable for the determination of 0.1 μg of iron in 0.01 ml: a 1% solution of the reagent in ethanol-chloroform (1 : 1) and a color filter with a maximum at 570 m μ were used. When more than a few mg of sulfate or phosphate was present per ml, the latter reagent is to be preferred (see also ZIEGLER³²).

** The choice of this purification method was justified in a more extensive consideration of the problem²⁸.

*** Concentrated in a "Teflon" dish, by evaporation, following the method of THIERS *et al.*³³.

alkaline earth metals behaved similarly and the alkali metals slightly better). It is clear that the mixture 93-5-2 is to be preferred. Table III shows the complete separation with the mixtures selected above.

TABLE I
SEPARATION OF Co FROM Cu, Fe, Zn AND Pb
(Percentages found in the first acetone-hydrochloric acid-water eluant)

Metal	Eluant ^a					
	89-1-10 ^b	89-1-10	91-1-8	92-1-7	93-1-6	94-1-5
Co	0.0	0.1	0.3	0.4	1.4 ^c	36.5
Cu	99	77	89	96	98	99
Fe, Zn, Pb ^d	99	94	96	98	99	100

^a Volume percentages of acetone, hydrochloric acid and water respectively.

^b 10% 0.01 *N* potassium iodide instead of water.

^c Standard deviation 0.5.

^d Mean values for the 3 elements are given.

TABLE II
SEPARATION OF Mn AND Co FROM Ca
(Percentages found in the second acetone-hydrochloric acid-water eluant)

Metal	Eluant ^a							
	98-1-1	97-1-2	96-1-2	95-1-2	94-1-2	93-5-2	92-6-2	92-5-0
Mn	79	76	86	90	93	94	94	96
Co	90	89	93	94	95	97	97	98
Ca	1.5	<1	1.5	1.5	2.0	2.5 ^b	3.0	3.5

^a Volume percentages of acetone, hydrochloric acid and water respectively.

^b Standard deviation 0.6.

TABLE III
COMPLETE SEPARATION OBTAINED BY CATION-EXCHANGE
(in percentages)

Fraction ^a	Ion			Ion				Ion		Ion		
	AlO ₄ ³⁻	SO ₄ ²⁻	PO ₄ ³⁻	Fe ³⁺	Zn ²⁺	Pb ²⁺	Cu ²⁺	Co ²⁺	Mn ²⁺	Ca ²⁺	Mg ²⁺	Sr ²⁺
First effluent	96	96	96	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Washing liquid	2	3	4	0	0	0	0	0	0	0	0	0
93-1-6	<1	<0.5	<0.5	99	99	99	98	1.5	1.0	0	0	0
93-5-2				<0.5	<0.5	<0.5	2.5	97	94	2.5	1.5	2.0
2 <i>N</i> HCl and H ₂ O								<1	4	97	98	98

^a See procedure below; the 93:7 acetone-water contained none of the ions to an appreciable extent; less than 0.5 or 1.0% of the respective ions was found in the column after the final treatment with 2 *N* hydrochloric acid and water.

CONCLUSIONS

(1) The most important separations: Fe-Mn; Fe-Mo; Fe-Co; Cu-Co and Mn-Zn are all established. The trace elements are separated from the macro constituents and concentration is easily accomplished. No interfering complexes are introduced.

(2) Further separations of the groups Co-Mn and Fe-Cu-Zn-Pb are possible, *e.g.* by applying anion exchange to the evaporated eluants (concentrated hydrochloric acid).

(3) The solvent 93:1:6 acetone-hydrochloric acid-water (in fact 92-1-7) is better suited for the separation of copper and cobalt than that used by KEMBER *et al.*^{24,25} (89:1:10 of the same constituents), which is however excellent when potassium iodide is added to the water to give a 0.01 *N* solution.

(4) The behaviour of the molybdate is in contradiction with the results of SAMUELSON²⁹.

Recommended procedure

Wet-ash 1 g of air-dried material with 0.5 ml of sulfuric acid and an adequate amount of nitric acid using hydrogen peroxide or perchloric acid if necessary. Cool, and dilute to 100 ml. Fill the column (Fig. 1) with a slurry of Amberlite XE-100 in 0.5 *N* hydrochloric acid and wash with 10 ml of the 0.5 *N* acid and 10 ml of water successively. Adsorb the cations during 40-50 min (molybdenum is found in the eluate) and wash with 50 ml of 0.01 *N* hydrochloric acid during 20 min. Condition with 10 ml of 93:7 acetone-water during 5 min and elute Fe, Cu, Zn and Pb with 100 ml of 93:1:6 acetone-hydrochloric acid-water during 100-125 min. Elute Co and Mn with 100 ml of 97:5:2 acetone-hydrochloric acid-water over a similar period and regenerate with 20 ml of 2 *N* hydrochloric acid and 20 ml of water (eluting Na, K, Ca, (Sr, Ba) and Mg).

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SUMMARY

Cation-exchange materials and selective elution with acetone-hydrochloric acid mixtures are used to concentrate the constituents of biological ashes and to separate them into the groups: MoO_4^{-2} , SO_4^{-2} , PO_4^{-3} ; Fe^{+3} , Zn^{+2} , Pb^{+2} , Cu^{+2} ; Co^{+2} , Mn^{+2} ; Na^+ , K^+ , Ca^{+2} , Mg^{+2} .

RÉSUMÉ

Au moyen des échangeurs de cations et par des éluions sélectives, il a été possible de concentrer et de séparer divers constituants des cendres biologiques (Fe, Zn, Cu, Mn, Pb, Mo, Co).

ZUSAMMENFASSUNG

Es wird die Anwendung von Kationen-austauschern und selektive Eluierung mit Aceton-Salzsäure Gemischen beschrieben zur Konzentrierung und Trennung der Bestandteile biologischer Aschen in folgende Gruppen: MoO_4^{-2} , SO_4^{-2} , PO_4^{-3} ; Fe^{+3} , Zn^{+2} , Pb^{+2} , Cu^{+2} ; Co^{+2} , Mn^{+2} ; Na^+ , K^+ , Ca^{+2} , Mg^{+2} .

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