

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

II. SOLVENT EXTRACTION

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INTRODUCTION (CHOICE OF THE SYSTEM)

An extensive literature on the concentration and separation of metals by solvent extraction is available. Reviews have been given by MORRISON AND FREISER¹, BABKO AND ZHAROVSKI² and WEST AND MUKHERJI³. Extractions with organic nitrogen and phosphorus compounds have been reviewed by WHITE⁴. The (discontinuous) extraction technique has the advantage of simplicity and speed.

Concentration is easily accomplished, especially when solvents with a low boiling-point are used.

Separation from macro-constituents is readily achieved. Mutual separations can be obtained in two ways: (1) by the application of several successive extracting agents and/or solvents (WEST³) or (2) with one agent and one solvent only, but using masking-agents and/or different pH values. Of course in both cases, mutual interferences of the extracting or masking agents must be avoided. Thus it is evident that a universal reagent, made selective by changes in the pH, is to be preferred.

Precipitation, under the circumstances required by the extraction process, should be prevented. This is especially important with biological ashes and in general with all samples containing a large excess of inorganic macro-constituents. It forms the main objection against the extraction of the halide and thiocyanate complexes, as these procedures usually require a concentrated solution of the respective anion in which precipitations readily occur.

Combination of extractions with quantitative techniques such as flame photometry, spectrophotometry, neutron activation etc., offers no problem. Combination with spectrophotometry is simple when the extracted complex has a characteristic light absorption, while combination with radiometric techniques is feasible, for example, when a radioactive reagent can be used for the extraction, or when the extracted metal complex can be exchanged with a radioactive metal.

In general however, combination with radiometric techniques (and also with polarography, titrimetry, etc.) poses several problems. Either the reagent used for the extraction should not be extracted or it should easily be evaporated or ashed.

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(The metal complex itself should also easily be ashed). These requirements are a serious objection against the use of aliphatic amines, organic phosphorous compounds, 8-hydroxyquinoline and thenoyltrifluoroacetone.

Only the reagents acetylacetone and diethyldithiocarbamate were considered to fulfill all the requirements mentioned above. Trifluoroacetylacetone could have been used but was not readily available. Xanthate could be used instead of the dithiocarbamate, but it does not allow the extraction of manganese.

Acetylacetone is universal and allows separations to be made by means of pH adjustment. The reagent is coextracted (and in fact is often used itself as a solvent for the metal complexes), but it can easily be evaporated. Metal acetylacetonates can be ashed. The use of acetylacetone as a radioactive reagent is uneconomical as a large excess is required for the extraction*. Radio-exchange of metal acetylacetonates has been studied but without success so far⁵.

Diethyldithiocarbamate is also universal and allows separations to be made by means of pH adjustment. Only a small amount of the reagent is extracted. The metal complexes can easily be ashed. As a rather small excess of reagent is required, the application of the labelled diethyldithiocarbamate is feasible (and in fact has been used for the determination of cobalt⁶). The exchange of the lead from the lead diethyldithiocarbamate with labelled thallium(III) and the exchange of lead with ²⁰⁴Tl-diethyldithiocarbamate have both been applied for the determination of sub-microgram amounts of lead^{5,6}.

ACETYLACETONE

FREISER and his coworkers⁷⁻¹⁴ have been very active in this field. WEST³ used the reagent in combination with other extracting agents (including diethyldithiocarbamate) to achieve a systematical separation of a large group of metals. In general, discontinuous techniques were applied but extractions were never complete in one procedure, even when pure acetylacetone was used. Only molybdate and cobalt(III) were found^{9,12} to be extracted below pH 0.0; iron(III) and copper were extracted at pH 2.0, but for zinc, lead and manganese higher pH values were required; cobalt(II) and iron(II) were not extracted at all.

Experimental

Materials (see also part I)

Acetylacetone (Merck *p.a.*) was neutralised daily by shaking with one volume of 0.01 *N* sodium hydroxide. All chemicals were again of reagent grade.

Apparatus

Most extractions were carried out with the mixture 1:1 chloroform-acetylacetone in the pyrex glass shaking tubes shown in Fig. 1. Eight tubes were attached with chromium-plated clips to the platform of a home-made aluminium shaker (Fig. 2), the velocity of which could be regulated between 5 and 20 periods per minute. The

* Paper chromatographic separation of ¹⁴C-labelled metal acetylacetonates, which require only a small excess of the reagent, has been studied⁵ without success: traces of the labelled reagent adhered to the paper and gave rise to a variable background.

tubes were filled in position I (the upper meniscus should stand between C and C¹) and emptied in position II. All operations with radio-active solutions were carried out in a shallow trough made of polyethylene.

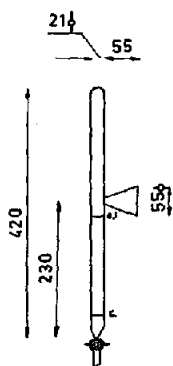


Fig. 1. Pyrex-glass shaking tube for discontinuous extractions.

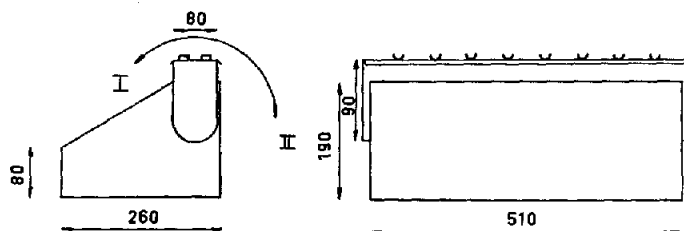


Fig. 2. Aluminium shaker for 8 tubes of Fig. 1.

Pretreatment of the sample

The ashing procedure was described in part I. Residues of perchloric acid had to be removed carefully here, as they interfered with the extraction (see STEINBACH¹²).

Analytical methods

The same methods were applied as in part I. For iron(III), flame photometry^{15,16} or spectrophotometry of the extract can replace the tracer method. The methods of MARONI AND DUBOIS¹⁷ and of CARTLEDGE¹⁸, for the spectrophotometric determination of copper and manganese acetylacetonates respectively, were found to be unsatisfactory. Thus copper was determined as described in part I (after the evaporation and ashing of the extract).

Results

Molybdenum was extracted from 6 *N* sulfuric acid (pH 0.8). As 0.5 ml of concentrated sulfuric acid was used for the ashing, the product had only to be diluted with 2.5 ml of water. With this small aqueous volume a small pill capsule made of PVC with a tightly fitting lid, and of diameter 25 mm and height 76 mm, was more convenient for the extraction. Pure acetylacetone was used instead of a mixture with chloroform, as it was more easily removed from the pill-case. With our procedure (see p. 134) two shakings sufficed for 98% extraction; less than 0.5% of the other trace elements was removed.

A similar result could be obtained for iron and copper at pH 2.0*. As the volume was increased by the neutralisation, either the pill-case (and pure acetylacetone) or the tubes shown in Fig. 1 (and acetylacetone-chloroform) could be used.

* All pH values given are starting values. The final pH values were either higher (below pH 5) or lower (above pH 5) than these starting values.

A pH value between 7.5 and 9.5 was required to obtain similar results for manganese and lead. These metals were not extracted below pH 4.0* and 6.0 respectively.

The extraction of zinc and cobalt was incomplete under all circumstances. Only 40% of the zinc was extracted (between pH 6.0 and 9.5) from a solution of the ash of 1 g of dry cow liver. The extraction from a pure zinc chloride solution was only slightly better. For the cobalt, oxidation to cobalt(III) proved to be necessary and was best carried out with hydrogen peroxide at a pH between 8 and 9; the extraction itself was most effective between pH 4 and 5. In contrast to pure cobalt solutions, the cobalt from sample solutions was extracted only very incompletely (about 50%).

Cobalt(III) was unstable below pH 3 and thus extraction below this pH was negligible; but once it had formed, the cobalt acetylacetonate was stable even to acids**.

In conclusion, the acetylacetone extraction of molybdenum, iron, copper, manganese and lead from the solution of a biological ash is feasible, but cobalt and zinc are extracted only to an extent of 50% or less.

DIETHYLDITHIOCARBAMATE

Studies with this reagent have been carried out by many authors and reviews have been published¹⁹⁻²³. Dialkyl, pyrrolidine and other derivatives have also been applied. In general these compounds do not have many advantages, but some are more stable to acids than diethyldithiocarbamate.

Experimental

(see also part I and Experimental p. 130)

All chemicals used were of reagent grade. Mercury solution: 0.1 M potassium sodium tartrate containing 160 μg of mercury(II) (as the nitrate) per ml, adjusted to pH 8.5 with sodium hydroxide. The ashing-procedure was as described in part I. Again radio-isotopes were applied to facilitate the evaluation of the results. Copper was determined spectrophotometrically with the reagent itself, following the method of CLULEY²³.

Results

Experiments were again carried out with the ash of 1 g of dry cow liver. The tubes shown in Fig. 1, aqueous and organic volumes of 20 and 10 ml respectively, and a 10-fold excess of diethyldithiocarbamate over the total of the heavy metals were used. To prevent precipitations, 0.2 M potassium sodium tartrate was present. With 2 shakings of 5 min each, copper, lead and cobalt were completely extracted at pH values up to 14, zinc only up to 13, and iron and manganese up to 9. Molybdenum was extracted only below pH 5. Separation of copper, lead and cobalt could be obtained by back-extractions with potassium cyanide (Cu), and mercury(II) followed by potassium cyanide (Pb)***.

* This is in contrast to STEINBACH¹², but in accordance with FREISER *et al.*⁹

** This extraordinary behaviour of cobalt was not clearly indicated by either STEINBACH¹² or FREISER *et al.*⁹

*** This technique was used by PŘIBIL *et al.*²⁵ for the spectrophotometric determination of microgram amounts of cobalt and by the present author⁶ for the radiometric determination of sub-microgram amounts of cobalt.

Separation of iron and manganese could not be obtained in a similar way however, although several masking agents were applied (including fluoride, pyrophosphate, citrate, sulfite, hydroxylamine, cysteine, cysteinamine and "Tiron"). As manganese would have to be determined in the presence of a large excess of iron (with most biological and many other samples), extractions with diethyldithiocarbamate alone were not satisfactory*.

COMBINATION OF ACETYLACETONE AND DIETHYLDITHIOCARBAMATE

Successive extractions with acetylacetone (at pH 2.0) and diethyldithiocarbamate led to a satisfactory procedure. Fortunately the extractions with the diethyldithiocarbamate were only slightly influenced by the presence of the acetylacetone. In Fig. 3 the latter results are shown.

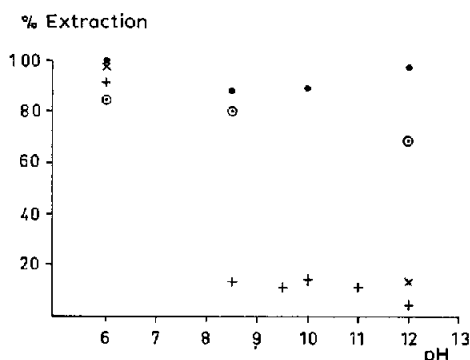


Fig. 3. Extraction of Mn (+), Pb (⊙), Zn (●) and Co (x) from biological ashes, with diethyldithiocarbamate and CHCl_3 (after the extraction of Fe and Cu with acetylacetone). Ammonium ion interferes with the extraction of Zn.

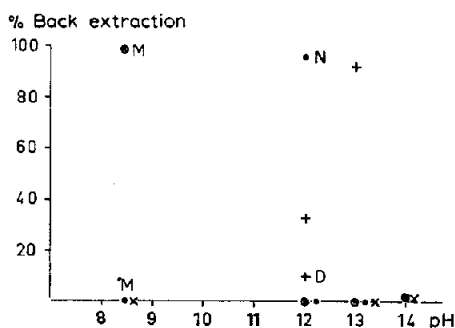


Fig. 4. Back-extraction of Mn (+), Pb (⊙), Zn (●) and Co (x) from the solutions of their diethyldithiocarbamate complexes in CHCl_3 with alkaline tartrate. M: Mercuric solution. N: Ammonia instead of sodium hydroxide. D: in darkness.

* Iron could be retained in the aqueous sample solution by adding sodium fluoride up to 0.1 N after the extraction of the zinc. In this way Mn could be separated from Fe. The determination of Fe in the aqueous fluoride solution was complicated appreciably however.

Unfortunately a separation into the groups lead-zinc and cobalt-manganese (by extraction at pH 12 for instance) is not possible: the amounts of the latter metals lost in the lead-zinc fraction are too high. (The behaviour of cobalt is not in accordance with the literature. This may be due to the combined influences of the acetylacetone and the constituents of our sample solutions.)

Thus extraction of all four elements at pH 6.0 was chosen and back-extractions at different pH values were carried out to achieve separation. These back-extractions are shown in Fig. 4.

Obviously the best separation is achieved by successive strippings at pH 13 (Mn), pH 14 (Zn) and pH 8.5 with the addition of mercury(II) (Pb). The mercury diethyldithiocarbamate can be removed with potassium cyanide while the cobalt complex remains in the chloroform.

PROCEDURE

Wet-ash and dilute with water to about 3 ml. Transfer to the pill-case and shake* during 2 min with 3 ml of acetylacetone. Centrifuge for 1 min at 1000 rev./min (\varnothing 25 cm) to promote separation and remove the upper layer with a pipet. Repeat this extraction once (the "film" between the two layers is left in the aqueous fraction). Evaporate the acetylacetone and treat the residue with some bromine water (Mo).

Transfer the aqueous layer to the tube of Fig. 1, adjust with ammonia to pH 2.0 (thymol blue) and dilute to 20 ml. Add 10 ml of 1:1 acetylacetone-chloroform and shake for 5 min, with a velocity of 10 periods per minute, in the apparatus of Fig. 2. Remove the extract, repeat the extraction, evaporate the combined organic layers and treat the residue with some bromine water or with a mixture 1:1 nitric acid-hydrogen peroxide (Fe, Cu).

Neutralise the aqueous layer to pH 6 (bromothymol blue), add potassium sodium tartrate to give a 0.1 *M* solution and diethyldithiocarbamate in a tenfold excess over the remaining trace elements.

Shake for 5 min with 5 ml of chloroform, remove the extract and repeat the extraction.

Transfer the combined extracts to a pill-case and strip the chloroform by shaking for 2 min with 5 ml of the following successive solutions: (1) pH 13, (2) pH 14, (3) pH 8.5**, (4) pH 8.5, mercury(II) (see p. 132) and (5) pH 8.5, 1% potassium cyanide, all solutions containing 0.1 *M* potassium sodium tartrate and adjusted to the desired pH with sodium hydroxide.

These solutions then contain: (1) manganese, (2) zinc, (3) no trace elements, (4) lead and (5) mercury. Cobalt remains in the chloroform phase.

CONCLUSIONS

The system chosen, a combination of acetylacetone and diethyldithiocarbamate, has some similarity with the extraction scheme of WEST³. For reasons which were discussed in the introduction, the extractions from acidic chloride and thiocyanate solutions, applied by WEST, had to be omitted. Furthermore our extractions with

* For instance in a "Microid Flask Shaker"

** Solution (3) is required to ascertain the right pH for solution (4); shaking with this solution for only a few seconds is sufficient.

acetylacetone and diethyldithiocarbamate were carried out at higher pH values and several strippings were used by us to separate the diethyldithiocarbamate complexes. By the above method, all metals, except iron and copper are separated. Concentration of the trace elements and separation from the macro-constituents is accomplished. The organic complexes which are introduced can easily be removed.

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SUMMARY

Extractions with acetylacetone and diethyldithiocarbamate are described. Through the successive application of these reagents the constituents of biological ashes are concentrated and separated into the groups: (1) MoO_4^{-2} , (2) Fe^{+3} , Cu^{+2} , (3) Mn^{+2} , (4) Zn^{+2} , (5) Pb^{+2} , (6) Co^{+3} and (7) Na^+ , K^+ , Ca^{+2} , Mg^{+2} , SO_4^{-2} , PO_4^{-3} .

RÉSUMÉ

Des extractions au moyen d'acétylacetone et diéthylthiocarbamate sont décrites, en vue d'une séparation des divers constituants des cendres biologiques (Fe, Cu, Zn, Pb, Mo, Co).

ZUSAMMENFASSUNG

Es werden Extraktionen mit Acetylacetone und Diäthylthiocarbamat beschrieben. Durch geeignete Anwendung dieser Reagenzien können die Bestandteile von biologischen Aschen in folgende Gruppen getrennt werden: (1) MoO_4^{-2} , (2) Fe^{+3} , Cu^{+2} , (3) Mn^{+2} , (4) Zn^{+2} , (5) Pb^{+2} , (6) Co^{+3} und (7) Na^+ , K^+ , Ca^{+2} , Mg^{+2} , SO_4^{-2} , PO_4^{-3} .

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