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A radiochemical procedure developed by the authors for neutron activation analysis of As, Cd, Cu, Sn and Zn in beef extract samples is described, based on combined precipitation steps to isolate the elements to be determined. Nuclides are separated with high degree of purity and good chemical yields. Interferences from threshold reactions are discussed and calculated. Results are shown for analysis of six samples.

Introduction

The growing interest about the presence of elements which either are toxic or become toxic when their concentration exceeds certain limits, in manufactured foods, has led to the fact that new specifications are required respecting their composition. Thus, for instance, the following upper limits have been demanded for concentration of some elements in beef extract: As: traces, Cd: 0.05 ppm, Cu: 10 ppm, Sn: 250 ppm, Zn: 100 ppm.

These elements may be well determined by neutron activation analysis. From the point of view of activation analysis, beef extract behaves like most of biological matrices, that is, their bulky activities are very similar, and radiochemical separation becomes necessary to isolate the nuclides to be measured. Several separation schemes have been proposed for multielemental analysis in biological material, which included the named elements.[1–5] However little work has been made in separation procedures only based on steps of selective precipitation. Such a technique was adopted by the authors to develop a method for simultaneous determination of arsenic, cadmium, copper, tin and zinc in beef extract.

Experimental

Sample and standard preparation

Filling of the irradiation ampoules was a somewhat difficult task, as beef extract has the characteristics of a sticky semo-solid mass. To accomphish that, the sample was charged into the body of a polyethylene syringe from the upper side, with the aid of a spatula. A polyethylene tube, sufficiently long as to reach the bottom of the ampoule, replaced the needle. With the piston returned to its original position, the syringe was exposed to the heat of a lamp so as to increase the fluidity of the loaded mass. Then, a little pressure, when applied to the piston, sufficed for allowing the mass to move along the tube and thus filling the ampoules. A mixed standard was prepared from Spec-Pure chemicals (Johnson, Matthey and Co, London) dissolved in Merck nitric and hydrochloric acids and bi-distilled water. The concentration (mg/ml) was: As, 0.0034; Cd, 0.0021; Cu, 0.579; Sn, 14.588 and Zn, 5.632. A measured volume of the standard was added to a sample weighed portion, 100 μl each 2 g sample; another weighing was performed and the mixture was thoroughly homogeneized. Finally, part of this mixture was weighed and sealed into a quartz ampoule in order to get a comparator for the sample when irradiating them together.

Irradiation

The samples were irradiated in one of the irradiation boxes of the RA3 reactor during 8 hrs. After a 48 hrs decay, quartz ampoules were washed with HNO_3 1 : 1; then with water, dried and finally cooled with liquid nitrogen before breaking them to start the separation.

Radiochemical separation

The attack of the sample was an oxidyzing one, performed by 15 ml of conc. HNO_3 and 2 ml of conc. H_2SO_4; 20 mg As, 20 mg Cd, 40 mg Cu, 40 mg Sn and 25 mg Zn carriers were added. The solution was filtered in order to remove fragments of the broken ampoule and then it was heated until complete removal of HNO_3. Afterwards the glass was cooled in an ice bath and 10 ml of conc. HCl were added slowly and with constant stirring. The residue left after HNO_3 elimination was then dissolved. A rapid 1 h stream of H_2S was passed while keeping the solution in the cold bath. Sulfides of As(V) and Cu(II) precipitated, the latter partially. The cold solution was let to stand for 1–2 hrs. The precipitate (A) was filtered, washed with 0.5N HCl and kept for arsenic and copper determination. The filtered solution was diluted with 230 ml of water and a stream of H_2S was passed until the sulfides of Cd(II), Sn(IV) and Cu(II) remained unprecipitated before)

were entirely precipitated. It was allowed to stand for 2 hrs. The precipitate (B) was filtered, washed with water saturated with H_2S and reserved for Cd, Cu and Sn determination. Zn was determined in the solution (C).

Precipitate (A) was treated with 10 ml of 2N NaOH and As_2S_5 was solubilized after a gentle heating, whereas CuS remained insoluble. The insoluble fraction (a) was filtered and washed with 5 ml of 2N NaOH, which were added to the solution (b).

Precipitate (B) was treated in a similar way to (A): SnS_2 was solubilized and the sulfides of Cd and Cu remained insoluble. This new insoluble fraction (c) was filtered and washed, as before, with 5 ml of 2N NaOH, which were added to the solution (d).

Arsénic. 1 ml of 30% H_2O_2 was added to the solution (b), which was then neutralized with conc. HNO_3 and a 5 ml excess was added. The solution was heated until dryness. The residue was dissolved with 20 ml of H_2O; 3–5 g of NH_4Cl and 10 ml of magnesia mixture were added. It was neutralized with 2.5% NH_4OH and precipitation of $MgNH_4AsO_4 \cdot 6H_2O$ was followed as indicated by VOGEL.[6] The precipitate was placed in a tared flask and measured; converted into $Mg_2As_2O_7$ by heating at 450 °C in a muffle and finally weighed.

Cadmium and copper. Precipitates (a) and (c) were joined and destroyed with a few ml of hot conc. HNO_3; the heating went on until dryness. The residue was dissolved in 50 ml of H_2O and ten drops of conc. HCl were added. The solution was filtered in order to remove the sulfur produced during HNO_3 attack. A stream of SO_2 was passed until saturation, so that Cu(II) was reduced to Cu(I) and 17 ml of a 2% NH_4SCN solution were added. The CuSCN precipitate was treated as recommended by HILLEBRAND et al.,[7] placed in a tared flask, weighed and measured.

Cd was determined as follows: 10 ml of 2% NH_4SCN were added to the filtered, which were then heated gently, both for removing SO_2 and for reducing its volume to half of the initial volume. The heating was turned more intense until the solution began to boil and $Cd(C_5H_5N)_2(SCN)_2$ was precipitated by adding 1 ml of pyridine. The precipitate was filtered and washed as indicated by VOGEL;[8] weighed and finally measured.

Tin. 1 ml of 30% H_2O_2 and 25 ml of conc. H_2SO_4 were added to the solution (d), which was heated to dissolve the SnS_2 precipitate. The solution was diluted to 250 ml with water and precipitation with cupferron was made following the technique described by FARNSWORTH and PEKOLA.[9] Tin was finally weighed as SnO_2 and measured.

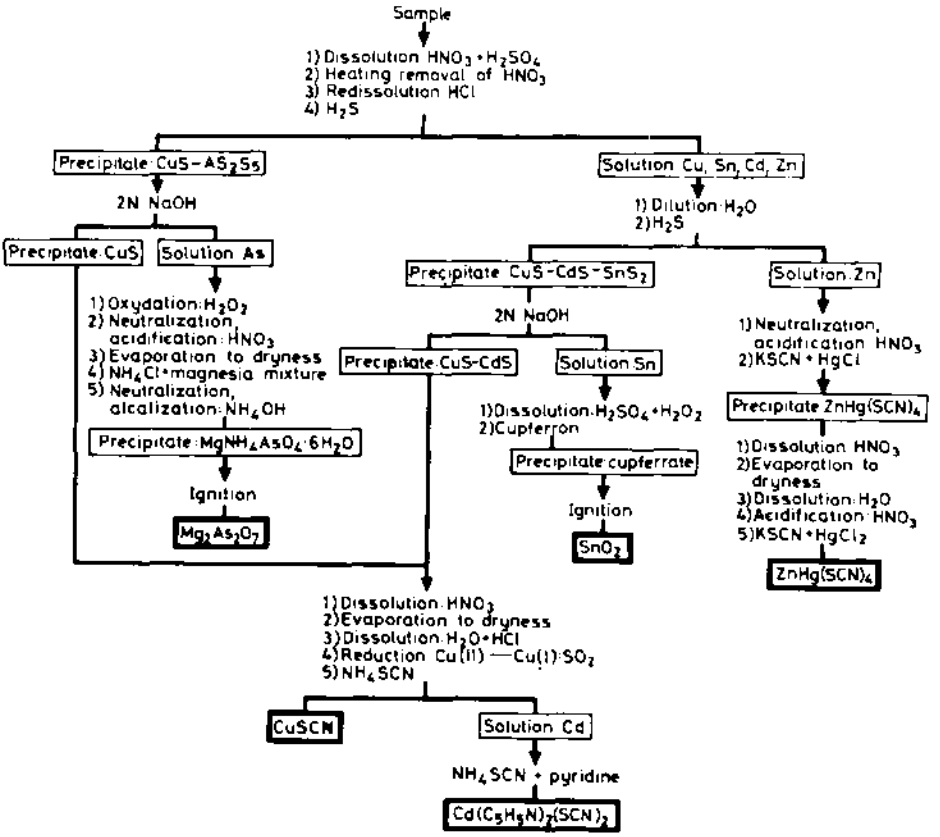

Fig. 1. Scheme of the separation procedure

Zinc. The volume of solution (C) was reduced to 50 ml by heating. It was neutralized with conc. NaOH; 0.5 ml of conc. HNO_3 were added and $ZnHg(SCN)_4$ was precipitated as recommended by HILLEBRAND et al.[10] The precipitate was filtered, washed and dissolved with 5 ml of conc. HNO_3. The solution was heated until dryness; the residue was dissolved with 50 ml of water, 0,5 ml of conc. HNO_3 were added and $ZnHg(SCN)_4$ was precipitated again. The precipitate was filtered, washed, dried, weighed and measured.

Remarks to radiochemical separation. The above procedure has been developed to isolate activities of interest from those produced by several interfering elements, mainly sodium, phosphorus and bromine. Little of them remained as occluded after

the first precipitation step performed for each element, being entirely removed when precipitating a second time. The situation is different when phosphate ions are occluded in arsenic sulfide precipitate, as they are also precipitated with magnesia mixture, then appearing as impurities in the amonium magnesium arsenate. The extent of this contamination is never so high as to introduce a serious error when determining chemical yield by weighing, but the undesirable background caused by ^{32}P bremsstrahlung can affect measurement of ^{76}As. Further purification, of needed, can be made by dissolving the amonium magnesium arsenate with conc. HCl, then diluting and precipitating the sulfide. Usually, this purification step is unnecessary.

Some other minor interfering elements tend to co-precipitate with sulfide precipitates, molibdenum and antimony being the most outstanding. The former accompany the arsenic sulfide precipitate, being dissolved when treating with 2N NaOH but not precipitated with magnesia mixture. The behavior of antimony is similar to that of tin; if present as Sb(III), it becomes precipitated with cupferron, so that it must be converted to Sb(V) prior to precipitation; the oxydizing step included in the procedure obviates this trouble, thus minimizing antimony interference.

Measurements and calculations. When developing the method, measurements were carried out with a high resolution Ge(Li) detector coupled to a 4096 multichannel analyzer in order to control the purity of the precipitates, without detecting any interference peak. Therefore such a high resolution detector was not, in fact, necessary to measure the samples but a NaI(Tl) one could be used, enhancing the efficiency as well. Measurements were performed with a well type NaI(Tl) detector (Harshaw, Integral Line), 10.6% resolution and 20.8% efficiency for 0.66 MeV gamma-energy of ^{137}Cs, coupled to a 4096 multichannel analyzer (Packard, model 2) operating to a 256 channels capacity. Measured precipitates were contained in glass vials of the type used in liquid scintillation counting.

The characteristics of the nuclides are listed in Table 1.

Concentrations were calculated by using the formula:

$$C = \frac{A_a}{A_b \frac{R_a}{R_b} - A_a \frac{m_b}{m_a}} \cdot \frac{W}{m_a}$$

where b, a – portions of the sample, with incorporated standard and without it;

C – concentration of the element (ppm);

A_b, A_a – activity of the nuclide (counts/min) in b and a (including decay corrections);
R_b, R_a – chemical yields for b and a;
m_b, m_a – masses of b and a (g);
W – mass of the element added to b (μg).

Peak areas were calculated by COVELL's method. Data smoothing was performed when measurement statistic was poor. When counting was unsufficient as to calculate concentrations, an estimation was made following criteria on detection limits given by ROGERS.[15]

Table 1
Nuclear data

Nuclide	Isotopic abundance,[a] %	Cross-section,[b] barn	Resonance integral,* barn	Half-life[a]	Measured gamma-energy[a]
^{76}As	100	4.4	44[c]	26.4 h	0.560
^{115}Cd	28.86	0.3	20.3[d]	53.38 h	0.336**
^{64}Cu	69.09	4.4	8.2[c]	12.70 h	0.511
^{117}Sn	14.30	0.006	0.49[c]	14.0 d	0.159
^{65}Zn	48.89	0.82	2.2[c]	244 d	1.115

*Normalized to a cut-off energy $\mu kT = 0.01$ eV.
**From ^{115m}In.
a,b,c,d Refs.[11-14]

Interferences

It has been mentioned that no interferences from nuclides other than those which were expected to measure appeared after chemical separation. Thus, in questioning if any interference could affect the analyses, the only possible alternative is that threshold reactions could lead to measured nuclides, considering as negligible second order interferences, such as they were calculated by OP DE BEECK.[16,17] The following formula may be used for estimating the magnitude of an interference by a threshold reaction.

$$[a]_{ap} = [i] \frac{M_a \Theta_i \Phi_f \bar{\sigma}_i}{M_i \Theta_a \Phi_{th} \frac{\sqrt{\pi}}{2} \sigma_a + \lambda I_a}$$

Table 2
Interference threshold reactions

Element	Main nuclear reaction	Interference nuclear reaction	Averaged cross-section,[a] mb	Isotopic abundance,[b] %
As	$^{75}As(n, \gamma)^{76}As$	1 – $^{79}Br(n, \alpha)^{76}As$	0.02 (c)	50.69
		2 – $^{76}Se(n, p)^{76}As$	0.63 (c)	9.0
Cd	$^{114}Cd(n, \gamma)^{115}Cd(\beta^-)^{115m}In$	3 – $^{115}In(n, n')^{115m}In$	188	95.7
		4 – $^{115}In(n, p)^{115}Cd(\beta^-)^{115m}In$	0.041* (e)	95.7
		5 – $^{115}Sn(n, p)^{115m}In$	0.13** (e)	0.35
Cu	$^{63}Cu(n, \gamma)^{64}Cu$	6 – $^{64}Zn(n, p)^{64}Cu$	31	48.9
Sn	$^{116}Sn(n, \gamma)^{117m}Sn$	7 – $^{120}Te(n, \alpha)^{117m}Sn$	0.13*** (e)	0.09
Zn	$^{64}Zn(n, \gamma)^{65}Zn$	none		

*$^{115}In(n, p)^{115m}Cd(\beta^-)^{115}In$ included.
**$^{115}Sn(n, p)^{115}In$ included.
***$^{120}Te(n, \alpha)^{117}Sn$ included.
a,b Refs.[10,11]
(c) Calculated.
(e) Estimated.

where a – element to be determined and i = interfering element, both producing the same nuclide;

$[a]_{ap}$ – apparent concentration of a;

$[i]$ – actual concentration of i;

M_a, M_i – atomic weights of a and i;

Θ_a, Θ_i – isotopic abundance of a and i target nuclides;

Φ_f – fast flux;

$\bar{\sigma}_i$ – averaged cross-section for threshold reaction;

Φ_{th} – thermal flux, $\Phi_{th} = n\,\bar{v}$, being n = neutron density and $\bar{v}$ = mean velocity of the Maxwellian spectrum;

G_a, I_a – thermal cross-section at v = 2200 m/s and resonance integral for (n, γ) reaction;

$\lambda = \frac{\Phi_{epi}}{\Phi_{th}}$; Φ_{epi} – parameter which defines the epithermal flux.

In order to make an a priori estimation about whether a threshold reaction may represent an important interference, it must be borne in mind that one, at least, of this two conditions has to be fulfilled: (a) the isotopic concentration of the interfering element is by far higher than that of the element to be determined or

Table 3
Results (expression for statistical errors: 68% confidence interval when referred to effective concentrations; 95% confidence limit when estimating detection limits)

S	As concentration, ppm · 10^{-3}	Cd concentration, $\times 10^{-3}$ ppm	Cu concentration, ppm	Sn concentration, ppm	Zn concentration, ppm
1	95 ± 8	nd: ul. = 4.2	0.87 ± 0.06	2.6 ± 0.2	12.4 ± 0.5
2	42 ± 1	nd: ul. = 5.2	0.59 ± 0.04	0.7 ± 0.1	11.1 ± 0.4
3	66 ± 3	d: $0.06 \leqslant c \leqslant 4.57$	0.51 ± 0.04	3.8 ± 0.2	10.9 ± 0.7
4	39 ± 4	nd: ul. = 9.6	0.60 ± 0.07	1.6 ± 0.3	18.8 ± 1.1
5	160 ± 10	nd: ul. = 4.1	0.78 ± 0.07	7.9 ± 0.5	13.9 ± 0.6
6	93 ± 5	nd: ul. = 6.5	0.91 ± 0.02	4.1 ± 0.9	14.0 ± 0.6

S: sample.
nd: not detected.
ul: upper limit.
d: detected.
c: concentration.

Table 4
Interference calculations

(a) Bromine interference

Sample	Br concentration, ppm	Apparent As concentration, ppm · 10^{-3}	Found As concentration, ppm · 10^{-3}	Interference, %
1	117 ± 4	0.024	95 ± 8	0.025
2	100 ± 4	0.021	42 ± 1	0.049
3	90 ± 3	0.019	66 ± 3	0.028
4	129 ± 4	0.027	39 ± 4	0.068
5	202 ± 5	0.042	160 ± 10	0.026
6	262 ± 6	0.054	93 ± 5	0.058

(b) Zinc interference

Sample	Zn concentration, ppm	Apparent Cu concentration, ppm	Found Cu concentration, ppm	Interference, %
1	12.4 ± 0.5	0.0067	0.87 ± 0.06	0.77
2	11.1 ± 0.4	0.0060	0.59 ± 0.04	1.02
3	10.9 ± 0.7	0.0059	0.51 ± 0.04	1.16
4	18.8 ± 1.1	0.0102	0.60 ± 0.07	1.69
5	13.9 ± 0.6	0.0075	0.78 ± 0.07	0.96
6	14.0 ± 0.6	0.0076	0.91 ± 0.02	0.83
Std.	5.632*	0.0030*	0.579*	0.53

*Expressed in mg/ml.
Data on RA3 fluxes:[19] $\Phi_{th} = 2.04 \cdot 10^{13}\ n \cdot cm^{-2} \cdot sec^{-1}$; ? = 0.0193
$\Phi_f = 2.1 \cdot 10^{12}\ n \cdot cm^{-2} \cdot sec^{-1}$.

(b) the cross-section for the threshold reaction reaches a significant value respecting to that of the main reaction.

Interference threshold reactions concerning the measured nuclides are tabulated in Table 2.

Accordingly to what was stated before, noticeable interfering effects may be expected in two reactions, those numbered 1 and 6; the possibility of occurring so in reactions 2, 4 and 7 seemed highly improbable. Regarding reactions 3 and 5, their interference can be considered as negligible, as they are referred to direct production of the short lived ^{115m}In (T = 4.50 h) which was almost entirely decayed when measuring samples.

Instrumental activation analysis was made for determination of bromine contents in the samples. Data obtained when determining zinc were used to ascertain zinc interference in copper determination. Results of these assays will be discussed later.

Table 5
Chemical yields

Element	As	Cd	Cu	Sn	Zn
Yield, %	65–85	45–55	65–90	50–80	60–80

Results and discussion

The described procedure has been applied to the determination of As, Cd, Cu, Sn and Zn in 6 beef extract samples. Results are listed in Table 3. The interference calculations (Table 4) which were performed as indicated before, show that bromine interference to arsenic determination is negligible in our case, not occurring the same respecting to zinc interference in copper determination, where significant interference factors have been found. However, measured copper concentrations may be considered as actual concentrations, for practical purposes, without too high an error.

The technique is suitable for routine analysis of a large number of samples, being realizable in a standard radiochemical laboratory. Good yields are attained (Table 5) and nuclides are isolated in a very high degree of purity. Detection limits are largely below concentrations fixed as upper limit for each element.

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