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Sensitivity of isotope dilution analysis is limited by the
method used for determination of the recovered mass of the
labelled element added as tracer /gravimetry, for instance/.
Determination of this mass by activation analysis increas-
es sensitivity of isotope dilution. This method is applied
to the analysis for copper, at ppb level, in analytical
grade reagents.

INTRODUCTION

Activation analysis of reagents faces some problems that

other techniques may ignore. The importance of these problems

has already been stressed by Becker and Smith[1]. In general,

these reagents are corrosive liquids requiring special care for

irradiation. Some of them may be decomposed by radiolysis form-

ing gases with a consequent build-up of pressure, which may

cause rupture of irradiation capsules or spillage of irradiated

liquids on opening the irradiation container. Effects of nuclear

bombardment, such as nuclear recoil and γ-heating, may enhance

the introduction of contamination from the container into the

reagent samples and may increase the rate of exchange of impuri-

ties between sample and container.

The number of papers on the determination of trace ele-

ments in reagents, by activation analysis, is not large, probab-

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ly because of the difficulties mentioned. Allina and Otwinowski[2] have determined, by activation, copper in reagents by evaporating about 10 ml of reagent and irradiating the residue; the sensitivity of the method is reported as being 10^{-4} µg. Jaskólska et al.[3] reported a sensitivity of 10^{-3} µg for the analysis of copper in hydrochloric acid, nitric acid and hydrogen peroxide.

A method that would keep the characteristic sensitivity of activation analysis, without the problems mentioned in connection with direct irradiation of those special samples, might be a good alternative for activation analysis. Isotope dilution, followed by activation analysis of the recovered element to be determined, may comply with the requirement of high sensitivity inherent in direct activation. Pauly et al.[4] were the first to use the association of these two techniques for the analysis of certain elements in a uranium alloy.

In the present paper this method is applied to the determination of copper in analytical grade hydrochloric acid, nitric acid, ammonium hydroxide and ammonium sulphide solutions.

EXPERIMENTAL

For the analysis of ammonium sulphide solution a volume of 20 to 40 ml of the reagent is treated with lead acetate solution[x] /5 mg Pb/ml/ and 2 ml of copper tracer solution /1 mg CuO irradiated in a thermal neutron flux of 10^{13} $ncm^{-2}sec^{-1}$ for 8 hours; the oxide is dissolved in nitric and hydrochloric acids and diluted to obtain 0.03 µg/ml of labelled copper/. The precipitat-

[x] The content of copper in the solid lead acetate can be determined by direct activation.

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ed lead sulphide, carrying copper with it, is aged for 30 min.
and filtered under vacuum using a chimney funnel glass apparatus.
The precipitate is washed three times with 2 ml of water each
time /deminerilized water then distilled twice in a quartz appa-
ratus/, dried under infra-red heat, placed in polyethylene en-
velopes and counted at the photopeak of 0.51 MeV, in a 400-chan-
nel γ-spectrometer coupled to a 3" x 3" well type NaI/Tl/ scin-
tillator, giving B cpm. The same volume of tracer solution which
was added to the reagent to be analysed is counted at this time
giving A cpm; the chemical yield is r = B/A.

In order to determine the amount of copper that was co-
-precipitated with the lead sulphide, this last precipitate is
irradiated for one hour in a thermal neutron flux of about
10^{12} ncm^{-2}sec^{-1}; a standard of copper is also simultaneously ir-
radiated. After irradiation, 20 mg of copper carrier /nitrate/
are added to sample and standard which are then treated with
2 ml of concentrated sulphuric acid and enough nitric acid to
destroy organic matter from the filter paper. 20 ml of water
and 0.5 ml of ferric chloride solution /10 mg Fe/ml/ are added
and the ferric ion is precipitated with ammonium hydroxide. The
ferric hydroxide scavenger is filtered. Recovery of copper in
the filtrate is over 99%. To the filtrate 2 ml of zinc chloride
solution /10 mg Zn/ml/ is added and zinc and copper are preci-
pitated with ammonium sulphide. The precipitate is filtered,
washed with a hot 1:20 hydrochloric acid solution and counted at
the peak of 0.51 MeV giving B_1 cpm.

The amount x of copper is calculated by the following expression, derived from the classical formula for isotope dilution[5]

$$x = \left(B_1 - B_t\right)M_s/A_s r$$

in which B_t is the remaining activity of the added copper tracer and which can be determined by counting an aliquot of the original copper tracer solution; M_s and A_s are the mass and activity of the copper standard irradiated together with the lead sulphide.

The analysis for ammonium hydroxide is performed similarly; the amount of copper found in the ammonium sulphide is subtracted from the copper found in the ammonium hydroxide.

For the analysis of hydrochloric and nitric acids, copper tracer is added to known volumes of these reagents which are gently heated to dryness. Concentrated ammonium hydroxide is added up to alkaline reaction, followed by the lead acetate solution, and lead is precipitated with 1 ml of the ammonium sulphide solution. From there on, the chemical procedure is carried out as in the analysis of ammonium hydroxide and ammonium sulphide solutions. The amounts of copper previously found in these two reagents are subtracted from the amounts found in the chemicals being analysed, i.e. hydrochloric and nitric acids.

RESULTS

Results are presented in Tables 1 to 4.

TABLE 1

Copper in analytical grade hydrochloric acid

Sample	Volume, ml	Cu µg	ppb
1	25	0.286	9.61
2	40	0.550	11.55
3	40	0.501	10.52
4	25	0.198	6.64
5	25	0.254	8.55
6	40	0.684	14.38
7	40	0.836	13.36
8	40	0.490	10.29
9	40	0.358	7.52

$\bar{x} = 10.3$, $s_x^x = 2.6$, $s_m^{xx} = 0.9$

^{x} Standard deviation of a single result
^{xx} Standard deviation of mean.

TABLE 2

Copper in analytical grade nitric acid

Sample	Volume ml	Cu µg	ppb
1	40	0.720	12.85
2	40	0.490	8.75
3	40	0.518	9.25
4	40	0.572	10.21
5	25	0.327	9.34
6	25	0.303	8.66

$\bar{x} = 9.8$, $s_x = 1.6$, $s_m = 0.7$

TABLE 3

Copper in analytical grade ammonium hydroxide

Sample	Volume, ml	Cu	
		µg	ppb
1	25	0.217	9.54
2	40	0.361	9.91
3	40	0.364	10.00
4	40	0.288	7.92
5	40	0.306	8.40

$$\bar{x} = 9.1, \quad s_x = 0.7, \quad s_m = 0.3$$

TABLE 4

Copper in analytical grade ammonium sulphide solution

Sample	Volume, ml	Cu	
		µg	ppb
1	40	0.491	12.27
2	40	0.532	13.30
3	40	0.518	12.95
4	40	0.628	15.70

$$\bar{x} = 13.6, \quad s_x = 1.6, \quad s_m = 0.8$$

DISCUSSION

The accuracy and precision of the method have been discussed in another paper[6] in which copper was determined in gold samples. In the present paper it is seen that the method can be applied equally well for very low quantities of copper in analytical grade reagents.

Volumes of samples were of the order of 20 to 40 ml but it can be seen that volumes of 10 ml could be used since the amount of copper would be of the order of 0.1 µg, which is a mass that can be easily determined by this method. Direct activation, in the case of some reagents, have been applied by Allina and Otwinowski[2] using 10 ml samples, but submitting the sample to an evaporation procedure before irradiation. At such low concentration levels, corresponding to one to ten parts per billion, evaporation may lead to a loss of some elements. In the present paper evaporation of the reagents, when necessary, was carried out after the labelled copper solution had been added in order to carry the isotope dilution method. This will increase the total copper concentration avoiding possible losses by volatilization or by adsorption in the glass ware. Besides, isotope dilution method corrects for losses of the element being analysed.

Results presented in Tables 1 to 4 show that even at this sub-trace level the precision, as indicated by the standard deviations, is very good.

An inconvenience of the method, compared with direct activation analysis, is that the time spent for one set of analyses is longer than for classical activation analysis. However, the advantages gained in avoiding irradiation of dangerous liquids compensate for this longer time for analysis of these particular types of samples.

It is interesting to note that an analysis of a nitric acid with the same trade mark as that whose results are reported in Table 2, but taken from a bottle for general use in the laboratory, gave results corresponding to 235 and 223 parts per

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billion in copper, showing how easily reagents become contamin-
ated when no special handling care is adopted.

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SUMÁRIO

Em análise por diluição isotópica a sensibilidade fica limitada pelo método adotado para a determinação da massa recuperada do material marcado (gravimetria, p. ex.). A determinação daquela massa por ativação aumenta a sensibilidade do método de diluição isotópica. No presente trabalho determina-se, pela associação dos dois métodos, cobre presente em reagentes analíticos e no nível de partes por bilhão.