The Substoichiometric Determination of Gold in Iron by Activation Analysis

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Received February 5, 1969

Either copper(II) diethyl dithiocarbamate or zinc diethyl dithiocarbamate was applied as a reagent for the substoichiometric extraction of gold to its activation determination in iron. The separation was carried out either by the well-known direct substoichiometric extraction of gold or by the substoichiometric reextraction of the $Au(DDC)_2Cl$ compound from the medium of ethyl acetate into diluted hydrochloric acid. The gold in iron was determined over the concentration range 0.04—0.2 μg/g.

From the point of view of activation analysis, the determination of gold is one of the most convenient applications of this method. This element has a single stabil isotope ^{197}Au with a thermal neutron cross-section 96 barns from which the isotope ^{198}Au, having half-life period 2.704 days, arises [1]. The same reaction, giving raise to the isotope ^{198}Au, takes place with resonance-neutrons. The resonance integral is 1558 barns. Main resonance is at energy of 4.9 eV [2]. Considerable attention is paid to the gold determination by activation analysis in literature. That is due, in particular, to the interest in gold determination in geology and mineralogy as well as in biology and medicine owing to the biological importance of this element.

From the papers of recent years, both the studies on the substoichiometric determination of gold in chelate form by means of diethyl dithiocarbamates by activation analysis [3] or by isotopic dilution analysis [4], resp. and the studies on the substoichiometric determination of gold in a form of ion association aggregate [5] are remarkable.

In this paper, the determination of trace amounts of gold in iron is presented. This research was carried out in connexion with the metallurgical investigation, concerning the observation of gold concentration during the melting process in steelworks. Besides other methods described formerly [6], activation analysis was used for the determination of gold in iron.

To solve this problem some results of the paper [3], concerning the substoichiometric determination of gold in a form of chelate by means of extraction of diethyl dithiocarbamates (DDC), have been used. For a deliberate use of this reagent, the studies [7, 8] of extraction by means of diethyl dithiocarbamate have been very important because they render possible to elucidate some apparent inconsistencies between the papers [3, 4] and some earlier detailed studies of the extraction of diethyl dithiocarbamates [9, 10].

Experimental

Measuring equipment

1024-channel pulse-height analyser (INR ČSAV, Prague-Řež).
Ge(Li) detector of γ-radiation (INR ČSAV, Prague-Řež), active volume 20 cm³.
Counting rate meter NZQ 711T (Tesla, n. p., Přemyšlení).
Device for automatic extractive radiometric titration [11].

Reagents

Gold(III) chloride 10^{-2} M solution in 5 M-hydrochloric acid.
Copper(II) diethyl dithiocarbamate in chloroform.
Zinc diethyl dithiocarbamate in chloroform.
Zinc diethyl dithiocarbamate in ethyl acetate.
The reagents were prepared by mixing the water solution of commercial sodium diethyl dithiocarbamate, analytical reagent grade (Lachema), with the water solution of excess zinc sulfate or the ammoniacal solution of excess copper(II) sulfate and by extracting with respective solvents. The concentrations of reagents were 6×10^{-3} M, with respect to starting NaDDC.
Ethyl acetate, chloroform, and other chemicals were analytical reagent grade.

Irradiation

The samples of iron were wrapped up in aluminium foil and irradiated together with standards (0.1 μg Au in the form of evaporation residue in a sealed quartz-ampule) for 20 hours in active zone of reactor VVR-S (INR ČSAV, Prague-Řež). The neutron flux in active zone was 10^{13} n cm^{-2} s^{-1}. The samples were analyzed after a day's cooling approximately.

Radiometric titrations

Extractive radiometric titrations were carried out either according to paper [12] in a vessel by measuring γ-radiation by means of scintillation detector or by using a device for automatic extractive radiometric titration. For the elucidation of extraction properties of gold(III) diethyl dithiocarbamates, the following titration curves (Fig. 1) were used:

1. Gold(III) extraction from the medium of 1 N-HCl into chloroform by means of zinc diethyl dithiocarbamate (or the same with both copper(II) and mercury(II) diethyl dithiocarbamate).
2. Gold(III) extraction from the medium of 1 N-HCl into benzene by means of zinc diethyl dithiocarbamate.
3. Gold(III) extraction from the medium of 1 N-HCl and 0.1 N-$HClO_4$ into chloroform by means of zinc diethyl dithiocarbamate.
4. Gold(III) reextraction from ethyl acetate into 1 N-HCl by means of zinc diethyl dithiocarbamate.

The reagent solution in chloroform was used in the cases 1, 2 and 3 while the reagent solution in ethyl acetate was used in case 4.

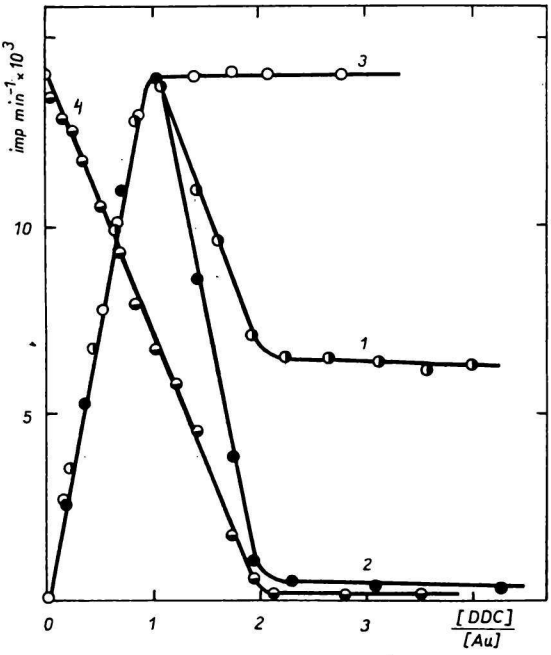

Fig. 1. Dependence of the change of gold activity (imp min^{-1} 10^3) in organic phase on the amount of diethyl dithiocarbamate added (expressed in molar ratio DDC/Au). The extraction systems used: *1.* chloroform—1 N-HCl; *2.* benzene—1 N-HCl; *3.* chloroform—1 N-HCl and 0.1 N-$HClO_4$; *4.* ethyl acetate—1 N-HCl. The volume of organic phase 30 ml, the volume of water phase 100 ml.

Development of the method

In addition to the well-known facts concerning the substoichiometric extraction of gold(III) diethyl dithiocarbamates, it was found that the amount of iron had no effect on the substoichiometric extraction of gold by means of diethyl dithiocarbamate considered that the sample, the weight of which did not exceed 1.5 g, was dissolved in mixture of HCl and HNO_3, evaporated with HCl nearly to dryness and the final solution adjusted to concentration of 1 N-HCl. EDTA had no influence on the extraction of gold and could be used for a successful masking of some contaminants. The proof of reproducibility of direct substoichiometric extraction was taken from the papers [3, 4] and [7]. The reproducibility of reextraction of a compound, the composition of which might be $Au(DDC)_2Cl$, from ethyl acetate fraction was investigated by continuous extractive radiometric titration of a solution containing gold(III) in ethyl acetate. It was found by observing the change of ^{198}Au activity in organic phase that the equivalent point corresponded in this titration to the molar ratio 1 Au : 2 DDC. The course of this titration is presented in Fig. 1 (curve *4*).

Results and Discussion

Diethyl dithiocarbamates are often applied in analytical practice as a selective reagent for several elements. According to earlier studies, they can not, however, be used for gold determination. The AuDDC compounds are said in reviews [9, 10] to be very little liable to extraction (about 30% by using tetrachlormethane as solvent). In spite of that, this reagent has been successfully used for the substoichiometric extraction of gold. The instability of reagent, which is usuelly delivered in the form of sodium diethyl dithiocarbamate, has been eliminated by transforming it into the stable complex $Cu(DDC)_2$ or $Zn(DDC)_2$ [3, 4] what allows to use it in acid solutions. The apparent discrepancies between the papers, published by *Bode* and *Neumann* [9, 10], and those by *Beardsley et al.* [3, 4] have been elucidated in the studies of extraction of gold(III) diethyl dithiocarbamates [7, 8]. Gold(III) forms successively two complexes with diethyl dithiocarbamates. The first one, hawing molar ratio 1 Au : 1 DDC (composition $Au(DDC)Cl_2$), comes into existence in a shortage of reagent while the second one, having molar ratio 1 Au : 2 DDC (composition $Au(DDC)_2Cl$), arises in the event of an abundance of reagent. The first compound has all properties of chelate, whereas the second one is an ionic association aggregate. This effects the poor extraction of gold into non-polar solvents when an excess of solvent is used. It can, however, be extracted in the event of reagent lack very well. Its extraction constant (not determined yet) is higher than that of mercury and copper so that these metalls may be replaced in respective chelates by gold easily. For this very reason, the diethyl dithiocarbamates of some metalls, such as zinc, copper, mercury etc., can be successfully applied for the gold determination. The selectivity of extraction increases with the increasing extraction constant of chelate used.

There is only one complex formed in the molar ratio 1 Au : 1 DDC when a solution with univalent complex linked gold ($KAuI_2$) is used. This complex can be extracted into chloroform easily.

If ClO_4^- ions are present in a solution of Au(III), the gold is extracted in univalent form apparently. In reality, two complexes are successively formed, like in the medium of HCl, of which the second one can be easily extracted into chloroform. In case the concentration of Cl^- ions exceeds the concentration of ClO_4^- by multiple, the compound $Au(DDC)_2ClO_4$ is formed in preference.

The fact that the chelate $Au(DDC)_2Cl$ can not be extracted into ether and ethyl acetate is very important for analysis. Under certain conditions, gold(III) is extracted as chloride complex into ethyl acetate nearly quantitatively [13]. By the extraction of chloride complex and substoichiometric reextraction, two successive and rather effective separation degrees can be attained. The titration curve (Fig. 1, curve *4*) of reextraction of gold(III) compound with diethyl dithiocarbamate is a sufficient proof of reproducibility of this procedure. The equivalence at molar ratio 1 Au : 2 DDC is apparently paradoxical. In this reaction, the starting gold complex $AuCl_4^-$ probably gives rise only to compound $Au(DDC)_2Cl$.

Two of the above methods have been applied for the determination of gold in iron. One of them (I) is the direct substoichiometric extraction in which gold is extracted immediately after solving the sample of iron with gold carrier and adjusting the hydrochloric acid concentration in solution. The second one (II) is more suitable for the samples of alloyed steels where the presence of other elements can cause the interferences of determination. It is based on the previous extraction of gold(III)

by ethyl acetate (or ether) and the subsequent substoichiometric reextraction of gold(III), performed after the washing of organic phase.

The working procedure of both methods can be divided in the general part and the part characteristic for the chosen method.

The general part is based on the dissolution of the sample of irradiated iron together with a carrier of gold in hot mixture of HCl and HNO_3 and on the filtration of the insoluble residue after washing with the same mixture. In the first method the filtrate has to be evaporated twice with hydrochloric acid nearly to dryness in order to remove the nitric acid and diluted to concentration of 1 M-HCl. In the second method the filtrate has to be diluted 4—5 times and the gold extracted in the form of chloride into ethyl acetate or ether and the organic phase washed up with 1 M-HCl. In both cases the gold is then extracted substoichiometrically.

The results of determinations are presented in Table 1.

Table 1

Results of the activation determination of gold in iron by the direct substoichiometric extraction of gold $Zn(DDC)_2$ into chloroform (method I) and the substoichiometric reextraction of gold $Zn(DDC)_2$ from ethyl acetate (method II)

No.	Method	Number of determination	Gold content in iron μg/g	Average error of arithmetic mean μg/g
1	I	24	0.189	0.003
2	I	24	0.158	0.001
3	I	18	0.144	0.002
4	I	18	0.169	0.002
5	I	18	0.177	0.002
6	I	18	0.170	0.002
7	I	18	0.182	0.002
8	II	2	0.052	0.001
9	II	2	0.041	0.001
10	II	2	0.046	0.001

In our case, the carrier of gold has been added in the amount of 2 mg, *i.e.* 1 ml of stock solution. The amount of the reagent added has corresponded to the 60% extraction of the gold carrier in sample. That means that 1 ml of reagent solution has been added when the first method has been used while 2 ml of reagent solution have been required for the same yield in case of the second method.

The author wishes to thank Ing. M. Křivánek, CSc., for his interest and helpful discussions during the course of this work.

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Translated by R. Domanský