Brief Communications

Reaction of acrichin with hexachloroantimonic acid and its analytic application

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The fluorometric reaction of acrichin (quinacrine hydrochloride) with hexachloroantimonic acid has been studied. The formation of a water-insoluble product has been shown. The precipitate contains equimolar quantities of acrichin and acid. The optimal conditions of formation, extraction, and determination were found. Acrichin was used for the extraction-fluorometry determination of nanogram amounts of antimony(v).

Key words: acrichin, antimony(v), extraction, fluorometric determination.

Morine, Safranine T, Rhodamines and other dyes have been suggested as fluorescent reagents for the determination of microgram amounts of antimony.[1] Low detection limits make the methods applying these dyes unique, but in most cases they are not selective enough. Al, Ga, Hf, Sn, Se, Th, Zr, V, Au, Fe, Ti, and Cr prevent the determination of antimony with Morine ($c_{\min}$ = 0.05 μg · mL^{-1}); Tl, Au, Ga, Fe, W, Ti prevent the determination of antimony with Safranine T ($c_{\min}$ = 0.015 μg · mL^{-1}). To increase the sensitivity and selectivity of antimony determination, it has been suggested to follow the extraction of its compounds with Crystal Violet by a second extraction with Ethylrhodamide C ($c_{\min}$ = 0.02 μg · mL^{-1}). This determination is difficult in the presence of Tl, Hg, Pt, Au. Acridine dyes are the more sensitive and selective.[2,3] Pd, Au, and Ga prevent the determination of antimony by Acridine Orange ($c_{\min}$ = 0.006 μg · mL^{-1}) and Rivane ($c_{\min}$ = 0.003 μg · mL^{-1}).

This work is devoted to the fluorescent reaction of hexachloroantimonic acid with a member of the acridine series, acrichin (9-[5′-(diethylamino)pentyl-2′-amino]-2-methoxy-6-chloracridine dihydrochloride).

The acrichinium cation, $C_{22}H_{30}N_3Cl^{2+}$ (ACC), forms stable complexes with complex anions of mercury(II), antimony(v), and other elements and was first suggested by us as a fluorescent reagent for the determination of microgram amounts of these elements.[4,5]

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Experimental

An antimony solution was prepared by dissolution of a weighed amount of antimony(v) chloride (chemically pure) in 9.0 *M* HCl. The titer of the solution was measured iodometrically. The solution of acrichin was prepared by dissolving a weighed amount of pure reagent in distilled water. The solutions to be tested were prepared by diluting aliquot parts with water or with aqueous solutions of HCl having the required concentration.

The equilibrium pH value of the water phase was measured by a glass ESL-PG-04 electrode with the use of a pH-262 potentiometer. The optical densities and absorption spectra of extracts were registered on a Perkin-Elmer-Coleman 575 spectrophotometer; the intensity of fluorescence and the fluorescent spectra were recorded on a Perkin-Elmer MPF-43 spectrofluorometer.

A number of organic solvents were examined to choose the optimal solvent extracting the maximum quantity of ACC hexachloroantimonate with minimal extraction of the simple salt of the reagent (Table 1). An equal volume of different solvents was added to water solutions containing equal amounts of antimony(v), acid, and ACC. After stirring for a minute and phase separation, the intensity of fluorescence in the organic phase was measured. The standard extracts were prepared similarly. The ratio between the differential intensity and the background fluorescence of extracts ($\Delta I/I_0$) served as the criteria for choosing the optimal solvent.

Results and Discussion

It has been stated previously[5] that the ACC cation reacts with the hexachloroantimonate ion to form the compound ACC hexachloroantimonate, which is insoluble in water, colored, and fluorescent and is easily extracted by organic solvents. This compound is referred to as an outer-sphere complex.[6–8]

As can be seen from Table 1, 1,2-dichloroethane is the best extragent among the solvents examined. In the case of this solvent, the extracts demonstrate not only a high value of the intensity of differential radiation but also a low value of background radiation. In further research 1,2-dichloroethane was used as the extractor. The absorption spectra of the dichloroethane extract of ACC hexachloroantimonate recovered were measured in the region of 300—600 nm. In this region of wavelength there are three maxima (451, 427 and 347 nm) in the absorption spectra of the dichloroethane extracts. In the fluorescence spectrum the maximum lies at 498 nm. The spectra of water solutions of acrichin (0.9 *M* HCl) are very close to those of these extracts.

Table 1. The dependence of fluorescent intensity of the ACC hydroxychlorantimonate extracts (ΔI) on the nature of the organic solvent

Extragent	ΔI	$\Delta I/I_0$
1,2-Dichloroethane	100	84.0
Chloroform	81	18.0
Ethyl acetate	21	7.7
Amyl acetate + acetone (4:1)	31	2.7
Butyl acetate + acetone (4:1)	22	2.6
Amyl acetate	23	2.5
Butyl acetate	17	2.3
Isoamyl acetate + acetone (4:1)	36	1.7
Isoamyl acetate	32	1.3
Carbon tetrachloride	0	0.0
o-Xylol	0	0.0
Toluene	0	0.0
Benzene	0	0.0

Note. c_{HCl} = 0.9 mol · L^{-1}; l = 1 cm; c_{Sb} = 3.29 · 10^{-5} mol · L^{-1}, c_{ACC} = 1.1 · 10^{-4} mol · L^{-1}, c_{Cl} = 2.0 · 10^{-2} mol · L^{-1}

The dependence of the fluorescent intensity of extracts of hexachloroantimonate with ACC on the acidity of the water phase was studied from pH 7 to the pH 8.5 *M* HCl solution. The differential intensity of fluorescence of the extract was found to be maximum and constant between 0.2 and 1.6 *M* HCl. Further exctractions were carried out from 0.9 *M* HCl solutions (Fig. 1). It was found earlier[9] that the hexachloroantimonate ion hydrolyzes under such conditions to form the $[Sb(OH)_4Cl_2]^-$ ion, which is transferred into the organic phase by common dyes. Therefore, we believe that in the presence of ACC the corresponding ACC hydroxychloroantimonate is extracted.

Extraction from water phases having optimal acidity and constant amounts of antimony and chloride ions but different amounts of dye showed that the recovery of ACC hydroxychloroantimonate is maximum when there is not less than a twofold excess of dye in the water phase.

The extraction equilibrium is reached after stirring for one minute. The recovery factor is determined for ACC hydroxychloroantimonate by repeated extraction with 1,2-dichloroethane provided that the optimal conditions are established. The first extraction provides a 0.96 recovery factor.

The ratio of the components in the compounds extracted, determined by Asmus' straight line method,

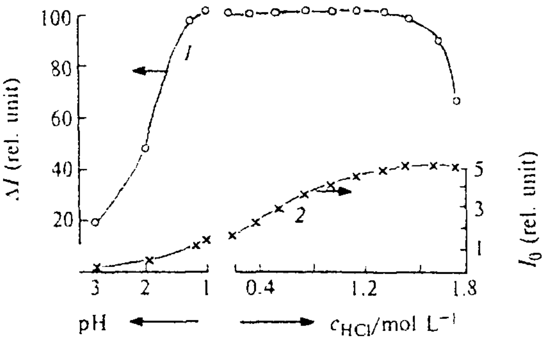

Fig. 1. The dependence of fluorescence intensity of ACC hydroxychlorantimonate (*1*) and reagent (*2*) on the acidity of the water phase: $V_{aq} = V_{org}$ = 1 mL; c_{Sb}= 5.0 · 10^{-5} mol L^{-1}; c_{ACC} = 2.2 · 10^{-4} mol L^{-1}; c_{Cl} = 2.0 · 10^{-2} mol L^{-1}.

isomolar series, and the Bent—French method,[10] is 1:1.

The extracts are stable and have low background radiation. The fluorescent intensity and optical density of the extracts remain constant for 5 days.

The detection limit of the extraction-fluorescence determination of antimony is evaluated relative to 3s-criteria (n = 20, P = 0.95) and is 2 ng/mL. The calibration curve is linear until the antimony content is 1.1 μg/mL at $c_{\text{ACC}} = 2.1 \cdot 10^{-5}$ mol · L^{-1}. The deviation of the calibration curve from linearity is due to the low content of dye rather than the concentration quenching of fluorescence. If the concentration of the dye in the water phase increases to $c_{\text{ACC}} = 2.1 \cdot 10^{-3}$ mol · L^{-1}, the upper detection limit of antimony determined can be increased to 100 μg/mL.

We developed not only this extraction-fluorescence method but also an extraction-photometry method for antimony determination with the use of acrichin. The sensitivity of this method is substantially less than that of the fluorometric method. The detection limit of antimony determination by the method of photometry is 0.35 μg/mL.

The following metals do not prevent the determination of 2 μg of antimony by the extraction-fluorescence method (in stoichiometric quantities): Mg, Ca, Sr, Ba, Al, Cd, Te$^{\text{IV}}$ ($5 \cdot 10^3$); Zn, Ni, Co$^{\text{II}}$ ($2 \cdot 10^3$); Sn$^{\text{IV}}$, Pb$^{\text{II}}$, V$^{\text{V}}$, Mo$^{\text{VI}}$ ($5 \cdot 10^2$); Cu$^{\text{II}}$, Ag (40); while Cr$^{\text{VI}}$, Au$^{\text{III}}$, Tl$^{\text{III}}$, and Hg$^{\text{II}}$ prevent the determination.

To conclude, an extraction-fluorescence method of antimony determination in nano- and microgram quantities has been developed. Its high sensitivity, selectivity, and low detection limit make this method different from the methods known. The high stability, both in water and organic solvents, of the complex formed makes the method quite applicable. The method is used for the analysis of metallic cadmium, tellurium, and sulfide ores from some fields.

References

1. F. F. Nemodruk, *Analiticheskaya khimiya sur'my* [*Analytical Chemistry of Antimony*], Nauka, Moscow, 1978, 222 (in Russian).
2. L. A. Grigoryan, Zh. M. Arstamyan, and V. M. Tarayan, *Zh. Anal. Khim.*, 1982, **37**, 629 [*J. Anal. Chem. USSR*, 1982, **37** (Engl. Transl.)].
3. L. A. Grigoryan, Zh. M. Arstamyan, and V. M. Tarayan, *Zh. Anal. Khim.*, 1984, **39**, 2039 [*J. Anal. Chem. USSR*, 1984, **39**, 11 (Engl. Transl.)].
4. L. A. Grigoryan, S. P. Lebedeva, R. G. Dayan, and R. A. Grigoryan, *Zh. Anal. Khim.*, 1990, **45**, 1762 [*J. Anal. Chem. USSR*, 1990, **45**, 1 (Engl. Transl.)].
5. L. A. Grigoryan, S. Musa, R. G. Dayan, K. V. Sarkisyan, and S. A. Avetisyan, *Uch. zap. Erevanskogo gos. univer.*, 1990, 2(174), 164 (in Russian).
6. V. V. Kuznetsov, *Usp. Khim.*, 1986, **55**, 1409 [*Russ. Chem. Rev.*, 1986, **55** (Engl. Transl.)].
7. L. A. Grigoryan, S. Musa, L. G. Gazaryan, and Sh. A. Markaryan, *Zh. Neorg. Khim.*, 1993, **38**, 1704 [*J. Inorg. Chem.*, 1993, **38** (Engl. Transl.)].
8. L. A. Grigoryan, A. B. Zolotoy, R. A. Grigoryan, S. K. Grigoryan, *Arm. Khim. Zh.*, 1994, **47**, 126 (in Russian).
9. V. M. Tarayan, Zh. M. Arstamyan, and L. L. Manucharyan, in *Uspekhi analiticheskoi Khimii* [*Analytical Chemistry Review*], Nauka, Moscow, 1974, 188 (in Russian).
10. M. I. Bulatov and I. P. Kalinkin, *Prakticheskoe rukovodstvo po photometricheskim metodam analiza* [*Handbook on Photometric Methods of Analyses*], Khimiya, Leningrad, 1986, 432 (in Russian).

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