Extraction of complex iodide anions with cationogenic tensides
Extraction spectrophotometric determination of divalent mercury

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This paper describes a new method of extraction of complex iodide anions based on their associates with the cations of cationogenic tensides in chloroform phase. The effect of the concentration of iodide and mineral acid on the extraction was studied. The extraction spectrophotometric determination of divalent mercury was developed as an example.

В работе описывается новый метод экстракции комплексных иодидных анионов, основанный на их ассоциатах с катионами поверхностно активных веществ в хлороформных растворах. Изучено влияние концентрации иодидов и минеральной кислоты на экстракцию. В качестве примера было разработано экстракционно-спектрофотометрическое определение двухвалентной ртути.

The complex iodide anions of some metals generally absorb radiation in the ultraviolet range. A number of these complexes are extracted into polar oxygen solvents and they can be extracted together with some basic dyes as ion associates into benzene, toluene, chloroform, *etc.* [1].

Since good results were obtained with the extraction of complex thiocyanate anions of some metals [2], *e.g.* molybdenum [3], cobalt [4], uranium [5], tervalent iron [6], tetravalent titanium [7], palladium and platinum [8], as well as the complex anion $[OsCl_6]^{2-}$ [9], and the complex anions of 12-molybdatophosphoric, 11-molybdatovanadatophosphoric acids and their reduction products (Molybdenum Blue) [10, 11], into a chloroform solution of 1-ethoxycarbonylpentadecyltrimethylammonium bromide, the present study is devoted to the extraction of complex iodide anions $[MI_x]^{(x-n)}$ — where n is the charge on the metal ion M. Among complex halides, these are most often used for the determination and separation of the individual metals.

Extraction of complex iodide anions, which are most stable in aqueous media [12], from a medium containing potassium iodide and sulfuric acid was carried out using a chloroform solution of 1-ethoxycarbonylpentadecyltrimethylammonium bromide, dimethyllaurylbenzylammonium bromide, and cetylpyridinium bromide. The first two substances exhibited the same extraction ability, while cetylpyridinium bromide was found not to be useful. The course of the extraction was simultaneously verified on the basis of the appropriate absorption spectra. Extraction with 1-ethoxycarbonylpentadecyltrimethylammonium bromide was studied in more detail; a chloroform solution of this substance has an absorption maximum at $\lambda = 246$ nm. Extraction of a mixture of this substance with sulfuric acid and iodide leads to a low absorbance at 360 nm as with dimethyllaurylbenzylammonium bromide — DLBB (Fig. 1, curve *1*). This extraction is dependent on the acidity of solution and is least in media of 0.03 to 0.12 M-H_2SO_4. It was found that the extraction is positive for Hg(II), Bi, Te, Sb(III), Tl(III), Ru(IV), Pt(IV), Pd, In, Sn(IV), Au(III), and Cu(II); the complex iodides of the latter four elements also have absorption maxima at 360 nm, but their absorbance is much greater than the blank. The following substances are not extracted: Cd, Sc, Ir, Rh, and Os. In Fig. 1 are depicted typical examples of extraction or the corresponding absorption curves and Table 1 gives a summary of all the studied elements, the λ_{max} values for the

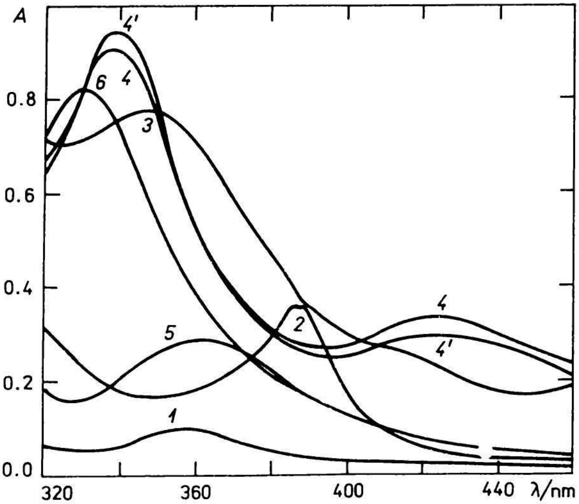

Fig. 1. Absorption spectra of complex iodide anions in the chloroform phase.
1. CPTB—KI—H_2SO_4; *2.* CPTB—PbI_4^{2-}; *3.* CPTB—BiI_4^-; *4.* CPTB—PdI_4^{2-}; *4'.* DLBB—PdI_4^{2-}; *5.* CPTB—RhI_6^{2-}; *6.* CPTB—HgI_4^{2-}.
$c_{KI} = 1$ mol dm^{-3}, $c_{H_2SO_4} = 1$ mol dm^{-3}, $c_{Me} = 1$ µg in 1 ml of organic phase, $c_{CPTB} = c_{DLBB} = 5 \times 10^{-3}$ mol dm^{-3}, $V_{water} = 25$ ml, $V_{org} = 10$ ml, $l = 1.00$ cm, measured against chloroform, time of extraction 1 min.

Table 1

Extraction of complex iodide anions with a chloroform solution of 1-ethoxycarbonylpentadecyltrimethylammonium bromide

Anion	λ_{max}/nm	$\frac{c_{H_2SO_4}}{\text{mol dm}^{-3}}$ *	$\frac{c_{KI}}{\text{mol dm}^{-3}}$
$[PbI_4]^{2-}$	388	1.0	0.1—0.25
$[SnI_4]^{2-}$	360	>12.0	>0.4
$[CuI_4]^{2-}$	360	>12.0	>0.4
$[HgI_4]^{2-}$	330	1.0	0.25
$[InI_4]^-$	360	6.0	>2.0
$[BiI_4]^-$	340, 486	1.0	0.05—0.5
$[SbI_4]^-$	340	1.0	0.5—0.75
$[AuI_4]^-$	360	>12.0	>0.4
$[TlI_4]^-$	350	1.0	>0.2
$[TeI_6]^{2-}$	555	6.0	>0.4
$[RuI_6]^{2-}$	340	1.0	0.25
$[PtI_6]^{2-}$	340, 400	1.0	0.1—0.25
$[PdI_4]^{2-}$	340, 420	1.0	0.05—0.25

* H_2SO_4 was selected as a general medium for the extractions studied.

particular ion associates with the cation of 1-ethoxycarbonylpentadecyltrimethylammonium along with the optimal concentrations of sulfuric acid and iodide for each element. Under the given conditions chloroform was found to be a suitable solvent for the tenside, especially as it does not extract the complex iodide anions alone. The described method involves rapid extraction and primarily the two phases separate rapidly, as was also found for extraction of complex thiocyanate anions [2].

Extraction determination of mercury

In a study of the extraction of mineral acids, *i.e.* hydrochloric, sulfuric or phosphoric, *i.e.* the blank, it was found that the latter is extracted minimally and thus the extraction of $[HgI_4]^{2-}$ was carried out from a medium containing 0.25 M phosphoric acid and 0.04 M-KI using 5×10^{-3} M-CPTB. It was found that the degree of extraction of mercury varies between 95.73 and 98.47% and the absorbance of the extract practically does not change during 1 h. The equation of the calibration curve was found by the least-squares method, $y = (0.0120 \pm 0.0030) + (0.1010 \pm 0.0003)\,x$, where y is absorbance and x is numerical value of the concentration of mercury in μg ml^{-1}. The Lambert—Beer law is valid in the range 0.05 to 16.0 μg Hg per ml of the organic phase.

Further, the interference from metals extracted as complex iodide anions was studied (Table 1) and it was found that the determination is not disturbed by a five-fold excess of Cu(II) and Te(IV), by a 50-fold excess of Au(III) and Tl(III) or by a 100-fold excess of Sb(V) or EDTA relative to a concentration of Hg 1×10^{-5} mol dm^{-3} in the extract. The determination of the same amount of Hg(II) is disturbed by the same concentration of Pd and by a 20-fold lower concentration of Bi. The complexing effect of EDTA can be employed to increase the selectivity of some of the determinations; *e.g.* it was found for Cu that Hg(II) can be determined in a ten-fold excess of this metal. Among the elements not extracted as the iodide, Hg(II) can, for example, be determined in a 1000-fold excess of Ca.

Experimental

Apparatus and reagents

A Pye-Unicam SP 8—100 recording instrument and a PHM-64 Radiometer pH-meter were used.

The stock 1.0 mg ml^{-1} mercury solution was prepared by dissolving 0.1616 g $Hg(NO_3)_2\cdot0.5H_2O$ and diluting with water to 100 ml. The solution containing 100 µg ml^{-1} Hg was prepared by successive dilution of the stock solution.

The 5×10^{-3} M 1-ethoxycarbonylpentadecyltrimethylammonium bromide (CPTB) solution was prepared by dissolving 1.006 g of the substance in chloroform and dilution to a volume of 500 ml.

10/3 M-H_3PO_4

All chemicals employed were of anal. grade purity. Redistilled water was employed.

Procedure

A sample solution containing 5 to 160 µg of divalent mercury is pipetted into a volumetric flask, 1.25 ml of 5 M-H_3PO_4 are added, along with 1 ml of 1 M-KI and the solution is diluted to a volume of 25 ml with redistilled water. The extraction is carried out for a period of 1 min with 10 ml of a 5×10^{-3} M chloroform solution of CPTB. After standing for 10 min the organic phase is separated and the absorbance of the extract is measured at 330 nm against blank solution ($l=1.00$ cm).

Conclusion

It follows from the study of the extraction of complex iodides or halogen anions that the most suitable extractant is chloroform, which does not extract the complex iodide anion alone but exhibits a marked maximum in the ($MeX_x^{(x-n)-}$, $CPTB^+$) ion associate spectrum after transfer to the organic phase (where X is I^-, Br^- or Cl^-). The extraction of the complex anions can be carried out from mineral acids, *e.g.* sulfuric acid with a minimum concentration 1 mol dm^{-3} (Table 1). It was found that the effectiveness of the extraction of mercury from the iodide medium is much greater than in case of bromide or thiocyanate media. Maximal extraction of iodide and other halogen anion complexes is ensured by a high concentration of cationogenic tenside in a nonpolar solvent, *i.e.* where the tenside exists in its micelle form. As an example of the new possibilities involved in extractions of this type, the determination of divalent mercury was studied. The determinable concentration range (0.5—16.0 $\mu g\ ml^{-1}$ organic phase) is by far the widest compared with other extraction methods (dithizone, cupral, mercupral).

References

1. Malát, M., *Absorpční anorganická fotometrie.* (Absorption Inorganic Photometry.) Academia, Prague, 1973.
2. Malát, M., *Fresenius' Z. Anal. Chem. 297,* 417 (1979).
3. Rančičová, M., Čuta, J., and Malát, M., *Vodní Hospodářství 31B,* 19 (1981).
4. Blažys, I. and Malát, M., *Chem. Listy 75,* 312 (1981).
5. Blažys, I. and Malát, M., *Collect. Czech. Chem. Commun.*, in press.
6. Adamec, F. and Malát, M., unpublished results.
7. Valcl, O. and Malát, M., unpublished results.
8. Nepimachová, B. and Malát, M., unpublished results.
9. Božkov, O., Čermáková, L., and Malát, M., *Anal. Lett. A12,* 1259 (1979).
10. Macháček, V. and Malát, M., *Microchem. J. 26,* 307 (1981).
11. Macháček, V. and Malát, M., *Rostlinná Výroba 27,* 991 (1981).
12. Zolotov, I. A., Ioffa, B. Z., and Chuchalin, L. K., *Ekstraktsiya galogenidnykh kompleksov metallov.* Nauka, Moscow, 1973.

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