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ANALYSIS*

**Separation and Preconcentration of
Trace Substances: Part IV**

**NEW TYPE OF FLOTATION OF
ION-ASSOCIATION COMPOUNDS OF
COMPLEXES OF MULTICHARGED
ANIONS WITH BASIC DYES**

(based on platinum metals as examples)

Prepared for publication by

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Separation and preconcentration of trace substances: Part IV — New type of flotation of ion-association compounds of complexes of multicharged anions with basic dyes (based on platinum metals as examples)

Abstract - Sparingly soluble ion-association compounds formed between multicharged anionic complexes (formed from trace amounts of an element to be preconcentrated and determined) and hydrophobic basic dyes, accumulate at the phase boundary after shaking with a solvent of low polarity. This type of flotation (without surfactant and gas bubbling) depends on the acidity, the dyestuff and the flotation agent. The separated compound can be determined with use of any suitable method. Combination of this separation technique with spectrophotometry allows a very sensitive determination, because 2-5 dye cations correspond to one atom of the element in the multicharged anion. Examples of separation and determination of the six platinum metals (1-10 µg) prove the effectiveness and precision of the proposed technique.

Multicharged anionic complexes, containing an analyte element, form sparingly soluble ion-association compounds with singly-charged cations of some basic dyes. These products are not extracted by nonpolar organic solvents but after shaking an aqueous solution with these solvents, the compounds accumulate at the phase boundary or adhere to the wall of the separatory funnel. After careful removal of both liquid phases and washing, the precipitate adhering to the wall of the separatory funnel can be dissolved in a small volume of a polar solvent (acetone, methanol, etc). In the solution obtained the isolated trace element can be determined by any suitable method. However because of the intense colour of the basic dyes it is of great advantage to combine the flotation separation with spectrophotometry.

The use of a term flotation for the technique described (ref. 1) is justified, because flotation consists of collecting solid particles, present in suspension, on the surface of gas bubbles or on organic solvent droplets in an aqueous phase. Accumulation and concentration of particles at the phase boundary is a common feature of flotation processes. The flotation of the present ion-association compounds takes place without addition of a surfactant, because they contain basic dyes with several aromatic rings, and thus form hydrophobic particles. The shaking of an aqueous suspension of the sparingly soluble ion-association compounds with a weakly polar organic solvent replaces the gas bubbling used in analytical precipitate or ion flotation with the participation of surfactants (refs. 2, 3). The present type of flotation can therefore be considered as a modification of precipitate flotation.

Numerous elements form multicharged anionic complexes able to associate with basic dyes. These include the anions of the heteropolyacids of silicon, germanium, phosphorus(V) and arsenic(V), the bromide complexes of bismuth and tellurium(IV), the thiocyanate complexes of molybdenum and tungsten, and the iodide complexes of cadmium. With suitable basic dyes all these anionic complexes form ion-association compounds which are the basis of very sensitive flotation-spectrophotometric methods for determination of these elements (ref. 4).

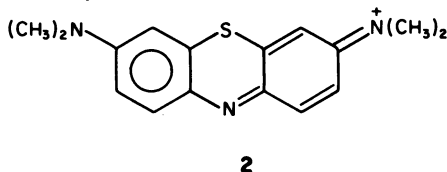
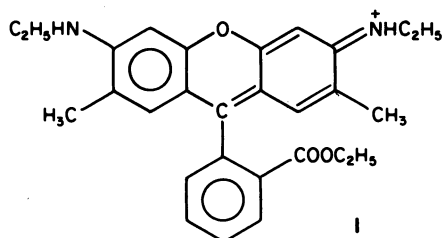
FLOTATION OF PLATINUM METALS IN TRACE AMOUNTS

Suitable anionic complexes and basic dyes

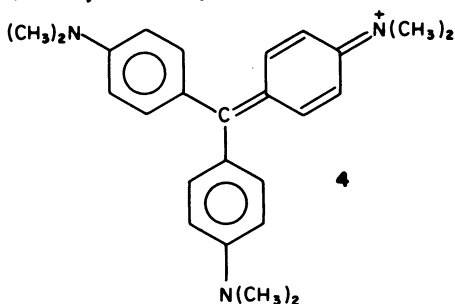
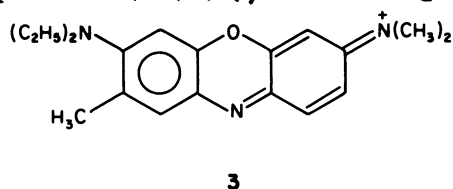
In hydrochloric acid (see Table 1), in the presence of tin(II), platinum metals form multicharged anionic complexes with platinum-tin bonds (ref. 5). For platinum, rhodium and iridium, their complexes with SnCl_3^- , and presumably also with chloride, have been found to be the most suitable for the formation of ion-association compounds with basic dyes for flotation purpose (refs. 6-11). Bromide and thiocyanate complexes have proved to be

useful for palladium (refs. 12, 13). Thiocyanate complexes were chosen for ruthenium and osmium because they enable the preliminary separation of these metals by extraction (refs. 14, 15); OsCl_6^{2-} has also been used, since this ion can easily be obtained by absorption of osmium tetroxide in sufficiently concentrated (8-10 M) hot hydrochloric acid (ref. 16). Relatively high ligand concentrations are necessary for rapid conversion of platinum metals into suitable anionic complexes. The concentration of tin(II) chloride should be 0.01-0.1 M for platinum, rhodium and iridium (refs. 6-11). The thiocyanate concentration should be 0.15 M for ruthenium and osmium, and only 0.02 M for palladium (refs. 13-15); the bromide concentration recommended for palladium is 0.2 M (ref. 12).

Xanthene, triarylmethane and azine dyes, are usually most suitable, and have often been used in chemical analysis (ref. 17). The methods referred to in Table 1 involve: rhodamine 6G (R6G) (1), methylene blue (MB) (2),



Capri blue (BC) (3), malachite green (MG) (4), and crystal violet (CV)



Rhodamine 6G, unlike rhodamine B, often leads to ion-association compounds that can be concentrated by flotation. The different behaviour of these two xanthene dyes is undoubtedly due to significantly weaker basic properties of rhodamine B, as a result of the presence of a free carboxylic group in the dye molecule. Dyes that exhibit more hydrophobic properties form floatable compounds more readily.

Formation and flotation of ion-associates

After shaking the aqueous pseudosolution of suitable acidity containing the ion-association compound, with an appropriate weakly polar solvent, and separating the phases, the sparingly soluble compound accumulates as a film at the phase boundary or adheres to the wall of the separatory funnel. Particles of the ion-association compound creep with the organic solvent up the wall of the separatory funnel. It is more favourable if the precipitate adheres to the wall because it makes it possible to remove both liquid phases from the separatory funnel without any loss of the ion-association compound. Principally, it depends on the flotation agent, as to where the sparingly soluble compound accumulates.

When the method of determination used after flotation does not require dissolution of the ion-association compound in a polar solvent, it is better for the sparingly soluble associate to accumulate as a film at the interphase of the two liquids. This makes it easier to remove the precipitate from the separatory funnel and to filter it off.

As well as the ion-association compound of the analyte metal, ion-association compounds with other anions in the solution (e.g. Cl^- , Br^- , SCN^- , SnCl_3^-) may be floated to some extent. However, the only systems which are of analytical interest are those in which such ion-association compounds can be completely washed away from the analyte ion-association compound. Generally, it is sufficient to wash the organic phase and the separated

TABLE 1. Flotation-spectrophotometric methods with basic dyes for determining platinum metals

Metal determined in system	Acidity during flotation	Floating agent (dissolution)	λ_{\max} (nm)	Molar absorptivity, ϵ $\times 10^{-5}$ $\text{l mol}^{-1} \text{cm}^{-1}$	Refs.
Pd-Br-R6G	pH 2-3	benzene (DMF)	530	3.50	12
Pd-SCN-MB	pH 1.5-3.5	benzene (acetone)	660	1.70	13
Pt-SnCl ₃ -CV	0.6 M HCl	benzene (ethanol)	585	2.10	8
Pt-SnCl ₃ -R6G	1 M HCl	DIPE* (acetone)	530	2.80	11
Rh-SnCl ₃ -R6G	2 M HCl	DIPE (acetone)	530	4.00	7
Rh-SnCl ₃ -MG	0.7 M HCl	DIPE (acetone)	627	3.40	6
Ir-SnCl ₃ -R6G	2.5 M HCl	DIPE (acetone)	530	3.60	9
Ir-SnCl ₃ -MG	0.5 M HCl	DIPE (methanol)	627	1.55	10
Ru-SCN-MB	pH 2-3	toluene (acetone)	655	2.20	14
Ru-SCN-CB	pH 2-3	DIPE (methanol)	630	2.70	15
Os-SCN-MB	pH 2-3	toluene (acetone)	655	2.20	14
Os-SCN-CB	pH 2-3	DIPE (methanol)	630	2.70	15
Os-Cl-R6G	1 M HCl	toluene (acetone)	530	4.00	16

* DIPE = di-isopropyl ether

precipitate 2-3 times with water or with a solution of the same acidity as used during flotation. The undesirable ion-association compound is decomposed, and the dye passes into the aqueous phase. Obviously, the analyte ion-association compound should not decompose during this treatment. In this way the absorbance of the blank can be decreased to 0.08-0.01.

For the formation of a suitable ion-association compound, and its quantitative flotation, an excess of the dye in the aqueous phase is needed, the amount depending on the system. The excess is small (10-15 fold molar excess with respect to the metal) in the systems such as Pt-SnCl₃-CV, Os-SCN-MB and Os-SCN-CB, it is greater (30-40 fold) for Pd-Br-R6G, Pd-SCN-MB and Pt-SnCl₃-R6G and is greatest (50-80 fold) for Ir-SnCl₃-MG and Ir-SnCl₃-R6G. Further increase of the dye concentration causes an increase of the blank absorbance.

Flotation of individual compounds has been examined over a wide range of acidity, from 6 M hydrochloric acid (or 3 M sulphuric acid) to pH 5. Each system has an optimal acidity range. As can be seen from Table 1, more acidic solutions (0.5-4 M HCl) are the optimal for SnCl₃ systems. For thiocyanate and bromide complexes, a low acidity (pH 2-4) is required. The optimal acidities for the formation of the anionic complex of the metal and for flotation are sometimes different (refs. 9, 10, 16). For example, for the Ir-SnCl₃-MG system, the optimal concentration of hydrochloric acid is 2.2 M for the formation of the complex and 0.5 M for flotation.

Of the weakly polar solvents the best flotation agents are di-isopropyl ether, benzene, toluene and xylene. It is worthwhile to note that the use of solvents lighter than water is advantageous (especially when washing; organic phase at the top). It seems that the symmetry of the solvent molecules is important for the flotation process. For example, the ion-association compound formed in the system Pd-Br-R6G (ref. 12) is floated by benzene or carbon tetrachloride, but not by toluene or chloroform. However,

it happens that solvents with less symmetrical molecules (e.g. toluene, xylene) are better flotation agents than the symmetrical benzene and carbon tetrachloride (ref. 16).

The necessary time of shaking of the aqueous phase with the flotation solvent is 15-60 s, depending on the system. Too long a shaking time results in higher blank values. In general, the aqueous phase can be much larger than the organic one (3-5 ml of floating solvent is sufficient).

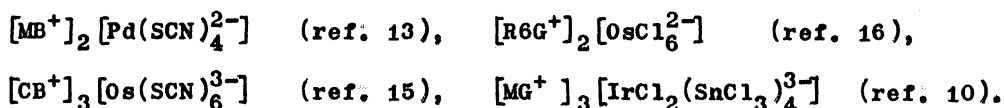
Acetone is the best polar solvent for the precipitates, which it rapidly dissolves. In some cases, methanol, ethanol and dimethylformamide have also been used. The volume of polar solvent for dissolution of the isolated compound can be as small, as 5-10 ml.

Composition of the floated compounds

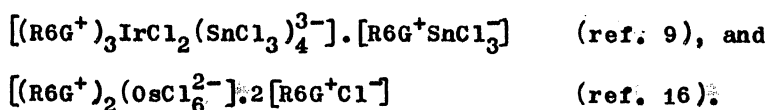
The dyes used have been of the best quality available, or were purified in the laboratory, generally by precipitation from ethanolic solution with a five-fold amount of diethyl ether.

The molar ratio of the metal to the dye has been established most often by comparison of the absorbances of the dye solutions themselves and their ion-association compounds dissolved in the same solvent. The method of isomolar series has also been used (refs. 6, 14, 15), and, in some cases, the logarithmic method has been applied (refs. 9, 12, 13, 16). The metal:ligand ratios in the anionic complexes have also been determined. Thiocyanate was estimated by determining sulphur by means of the methylene blue method (refs. 14, 15). Bromide was determined spectrophotometrically with methyl orange (ref. 12). The tin content was determined using phenyl-fluorone (refs. 6, 9, 10). Radioisotopes have also been used (^{82}Br , ^{113}Sn , ^{193}Pt and ^{192}Ir) (refs. 9, 11, 12).

On the basis of these studies and literature data on the formulae of the complexes of platinum metals with SnCl_3^- and Cl^- ligands (refs. 18-21), the ion-association compounds are suggested to be:



Considering the oxidation state of the metal and its coordination properties, it is supposed that some isolated compounds are adducts, composed of the ion-association compound of the metal complex and the dye cations, and the dye salt. Such adducts do not dissociate during washing. Examples of the proposed formulae of such adducts are:



Therefore, the metal:dye ratio varies from 1:2 to 1:5

- 1:2 - Pt (ref. 8), Pd (ref. 13), Os (ref. 16);
- 1:3 - Pd (ref. 12), Pt (ref. 11), Ir (ref. 10), Ru and Os (ref. 14);
- 1:4 - Rh (ref. 7), Ir (ref. 9), Os (ref. 16);
- 1:5 - Rh (ref. 6), Ru and Os (ref. 15).

For a given system the ion-association compounds have different compositions depending on the conditions (acidity, flotation agent). For example, for Rh-SnCl₃-MG, in 4 M hydrochloric acid medium, with benzene, the ion-association compound has a molar ratio of Rh:MG of 1:2, while in 0.6 M hydrochloric acid and with di-isopropyl ether this is 1:5 (ref. 6). In the system OsCl₆²⁻-R6G, for 1 M hydrochloric acid and toluene the ratio is 1:4 while at pH 2-4 and with xylene the ratio is 1:2 (ref. 16). In the system Os-SCN-CB, at the same acidity (pH 2-3), but using different flotation agents the ion-associates formed have various ratios of Os:CB - 1:5 in the case of di-isopropyl ether, and 1:3 in the case of toluene (ref. 15).

TABLE 2. Precision and accuracy data of the determinations of Pd, Ru, and Pt with flotation-spectrophotometric methods

Added (μg)	Found ^m (μg)	Standard deviation (μg)	Relat. stand. deviation (%)
<u>Palladium</u> (bromide and rhodamine 6G) (ref. 12)			
1.00	1.01 \pm 0.07	0.08	7.5
4.00	3.99 \pm 0.15	0.17	4.1
8.00	7.93 \pm 0.19	0.21	2.6
<u>Ruthenium</u> (thiocyanate and Capri blue) (ref. 14)			
2.00	1.96 \pm 0.11	0.13	6.5
4.00	3.94 \pm 0.15	0.17	4.2
8.00	8.04 \pm 0.15	0.17	2.1
<u>Platinum</u> (tin(II) chloride and rhodamine 6G) (ref. 11)			
4.00	4.07 \pm 0.10	0.13	3.2
8.00	7.92 \pm 0.17	0.10	1.3
12.00	12.20 \pm 0.21	0.09	0.8

^m For seven determinations, 95% confidence limits

Combination of flotation with spectrophotometry

The combination of the flotation of platinum metals with their spectrophotometric determination has resulted in spectrophotometric methods several times more sensitive than those previously available for the platinum metals. Table 1 presents the developed flotation-spectrophotometric methods and their characteristics. Additional sensitivity results from the fact that the volume of the polar solvent used for dissolution of the compound isolated can be much smaller than the volume of the initial aqueous solution.

Information about the precision and accuracy of separation and determination of μg -amounts of palladium, ruthenium and platinum by the proposed methods is given in Table 2. Beer's law is accurately obeyed.

Flotation-spectrophotometric methods are more selective than extraction-spectrophotometric procedures using basic dyes. There are many more ion-association compounds capable of extraction than can be floated. Only few other elements give ion-association compounds that can be floated under conditions favourable for the metal determined. With the proposed flotation-spectrophotometric methods, the platinum metals can easily be separated from almost all other elements.

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