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**Present and Future Status of
Organic Analytical Reagents – Part II**

**INORGANIC CHEMICAL ANALYSIS:
CLASSICAL METHODS, MOLECULAR
SPECTROSCOPY (ABSORPTION AND
EMISSION) AND SOLVENT
EXTRACTION**

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Present and future status of organic analytical reagents – Part II. Inorganic chemical analysis: classical methods, molecular spectroscopy (absorption and emission) and solvent extraction

Abstract - Following the general introduction to the present and future status of organic analytical reagents (OAR), a priori prognosis - a posteriori examination, aspects of inorganic chemical analysis are reviewed with emphasis on current practice, recent developments and trends. The technique areas included are qualitative tests, gravimetric and titrimetric procedures, solvent extraction and molecular absorption and luminescence spectroscopy in the UV-Visible region. Recent trends and developments noted are, in UV-visible absorption spectrophotometry - the use of micellar sensitisation; in luminescence - the use of low temperatures and chemiluminescent reactions; in solvent extraction - an increased interest in ion-association reactions, use of macrocyclic ligands, application of kinetic factors, solid-liquid and flotation systems.

CLASSICAL CHEMICAL PROCEDURES

The development and use of OAR in qualitative analysis established a large number of selective chemical reactions and spot tests for elements and their compounds. Their use in this connection gave rise to the concept of analytical functional groups whose usefulness was also shown during the search for new or improved OAR for quantitative analytical practice. A comprehensive literature is available (1-12).

The interest in OAR for gravimetric analysis was reduced with the fall in popularity of gravimetric procedures. A number of procedures however remain in use, particularly for reference analyses and for standardization. They are carried out in aqueous or mixed solvents where voluminous and not always pure precipitates of OAR complexes or chelates are formed. The excess reagent must be carefully washed from the precipitate before drying or removed by ignition. A low gravimetric conversion factor is of considerable advantage. Procedures requiring ignition of precipitates are less convenient (13-15). Among reagents still considered useful are biacetyldioxime, furildione dioxime or cyclohexanedione dioxime for the determination of nickel and palladium (16), 8-hydroxyquinoline (17, 18), for the determination and separation of various metal ions, N-benzoyl-N-phenylhydroxylamine (19) or α -benzoïn oxime (20-22) for the determination and separation of niobium and tantalum or molybdenum and tungsten.

The renaissance of titrimetric procedures just after the end of World War II arose from the ready availability of aminocarboxylic acids (complexans or chelons)

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as novel and universal titration agents for metal ions. Determinations with the most popular, EDTA, are still frequently used in routine laboratories or for the standardisation of metal ion solutions. The theory of complexometric titrations is well established (23 - 26), the titration end point can be evaluated with sufficient reliability to adopt such procedures even for micro-analysis (27). The advantages of complexometric titrations stimulated the development of new OAR as metallochromic (metal) indicators. Detailed texts, manuals and numerous critical review articles deal with the reactions of chelons, complexometric titrations (28 - 30) and metal indicators (31, 32).

MOLECULAR ABSORPTION SPECTROSCOPY IN THE UV-VISIBLE REGION

The most popular and widest range of application of OAR has been in spectrophotometry and solvent-extraction spectrophotometry in the UV-visible region for applied inorganic analysis. The most sensitive spectrophotometric methods are based on binary, ternary or even quaternary complexes, chelates or ion-pairs (ion-association complexes) of metals or non-metals, especially with dye OAR. Most procedures are of limited selectivity and need prior separation of the analyte or sophisticated masking of interferents. Molecular absorption spectrophotometry (UV and visible) is still among the most popularly used methods for the determination of Be, Sc, Ti, Zr, V, Nb, Ta, Mo, W, Re, platinum metals, U, Th and also often for lanthanoids, B, Al, Ga, In, Tl^{III}, P^V, As^V, Si, Ge, Se^{IV}, Cr, Sb, Bi and Mn. The most suitable OAR for spectrophotometric determination of metals and non-metals have been the subject of detailed discussion and review (33 - 50). Sensitive and selective determinations of Zr, Nb, Ta, V^V, lanthanoids, actinoids or platinum metals may be carried out on the basis of inner sphere ternary complexes (51). The interference of absorbing matrix background or reagent excess may be removed by difference (52, 53), derivative (54) or dual-wavelengths spectrophotometry (55, 56).

OARs also play an important role in the simultaneous multielemental spectrophotometric analysis as often there are sufficient differences between the spectra of particular components (eg metal chelates of polyphenols (57 - 59), dithiocarbamates (59, 60), N-heterocyclic azo dyes (61 - 64)). Various mathematical procedures are available to deal with mutual interactions of components (59). There are good long term prospects for multielemental analyses by using mixtures of reagents showing similar sensitivity for various analytes whose OAR chelates or other products have different spectrophotometric properties (mixtures of 1,10-phenanthroline and cuproine derivatives or ferrozine and cuproine derivatives for simultaneous determination of Fe^{II} and Cu^I (64 - 66), or 1,10-phenanthroline, neocuproine and sulphanilic acid and 1-naphthylamine for the determination of Fe^{II}, Cu^I, and NO₂⁻ (65)).

The spectrophotometric evaluation of analytes during their flow injection analysis is commonly based on absorbing OAR chelates (67 - 69). Kinetic factors in the flow system may, however, influence the composition and the optical properties of the reaction products. The simultaneous spectrophotometric determination of several elements may also be carried out in flow systems using a FIA analyzer containing a diode array and controlled by a micro-processor (70).

Micellar sensitisation has been widely exploited for metal chelates with selected dye OAR containing several acidic groups such as triphenylmethane dyes having a salicylic acid or catechol functional group in the molecule [eg Chrome Azurol S(C.I. 43 825), Eriochrome Azurol B(C.I. 43 830), Eriochrome Cyanine R(C.I. 43 820) or Catechol Violet) or xanthene dyes (9-substituted 2,6,7-trihydroxyxanthen-3-one Pyrogallol Red, Bromopyrogallol Red)] in the presence of various cationic or non-ionic surfactants or surfactant mixtures. Species formed in such systems have high molar absorptivities ($\epsilon > 1.0 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$) and considerable colour contrast, especially for Be, Al, Sc, Y, La, lanthanoids, Ga, In, Cu, Fe^{III} , UO_2^{2+} and Th. The concentration of the dye reagent and surfactant and also the optimum pH value are critical and different for each particular system. The nature of the reactivity in the presence of surfactant has not always as yet been completely elucidated. Stoichiometric ion associates of limited solubility are formed in aqueous solution for submicellar concentrations of surfactant and soluble complexes of various structures and stoichiometry. Complicated competition equilibria may take place in solutions with large surfactant or reagent excess, dependent on the concentration of components and on pH. Such complicated relations often result in curved calibration plots (eg 47, 71 - 79). In addition various sparingly soluble metal chelates may be solubilized in aqueous medium by addition of non-ionic surfactants, eg 1-(2-pyridylazo)-2-naphthol chelates in the presence of Triton X-100, and the extraction into organic solvents may be omitted. The same is true for sparingly soluble high molecular weight ion pairs such as those of 12-heteropolyacids with basic dyes in the presence of non-ionic surfactants (80 - 83).

LUMINESCENCE PROCEDURES

Binary and ternary complexes or chelates of OAR containing oxygen or nitrogen donor atoms having rigid structures may show intense fluorescence. Examples are complexes involving reagents such as polyhydroxy-flavones, 8-hydroxy-quinoline and its analogues, hydroxyarylhidrazones, benzoin, phenolcarboxylic acids, 2-hydroxy-3-naphthoic acid, polyphenols, hydroxy- and aminoxanthene dyes, o,o'-dihydroxyazo dyes, calcein and others forming fluorescent chelates with metal and non-metal ions whose outer electronic shell is s^2p^6 or $s^2p^6d^{10}$ [Al^{III} , Ga^{III} , In^{III} , Ca^{II} , B^{III} , Zr^{IV} , Hf^{IV} , Th^{IV} , Sc^{III} , Ge^{IV} , Sn^{IV} , Zn^{II} , La^{III} , Y^{III} , lanthanide^{III}s (84 - 86)]. OAR chelates of terbium and europium are an especially suitable basis for their fluorimetric determination (87 - 90). Various ion pairs or ion association complexes of rhodamines and other xanthene dye cations with colourless anionic metal or non-metal complexes may be evaluated fluorimetrically after their extraction into oxygenated solvents (91).

Low temperature luminescence has enabled increased sensitivity and even selectivity for the determination of certain metal ions and has created renewed attention to OAR at the present time (92, 93), eg lumogallion for the determination of niobium (94), 8-hydroxyquinoline for niobium (95), salicylic acid for boron (96), dibenzoylmethane for boron (97) or beryllium (98) and 2,3-diaminonaphthalene for selenium (99). Different quasilinear fluorescence spectra of various metal ion chelates, eg with polyhydroxyflavones or azomethines for the determination of Ga,

In, Al, Be, and Cd, being fixed in the crystal lattice of frozen aliphatic hydrocarbons (n-hexane, n-octane, n-pentane) enable selective determinations of several analytes, the high quantum yields of luminescence cause considerable sensitivity increase over solution measurements (100, 101). Recently, the enhancement of fluorescence in micellar solutions of non-ionic surfactants (eg for metal ion chelates of poly-hydroxyflavones or some 2,2'-dihydroxyazo dyes (102 - 105)) has been successfully used for analytical purposes. Room temperature phosphorescence in micellar solutions of surfactant (MS-RTP) in the absence of oxygen is of interest for selected metal ion OAR complexes (106). In addition, differences in luminescence life times at low temperatures of various metal ion chelates with particular OAR in mixture decrease mutual interferences (97, 107).

The chemiluminescence of certain OAR may also be exploited for analytical purposes. Luminol (3-aminophthalic acid hydrazide), lucigenine (10,10'-dimethyl-9,9'-biacridinium dinitrate) or lophine (2,4,5-triphenylimidazole) used for the determination of traces of activators or oxidants (108). Rhodamine B (C.I. 45 170) is a valuable substrate for the chemiluminescence of ozone (109, 110) and luminol for the determination of nitrogen dioxide (111).

SOLVENT EXTRACTION

The extraction of cations and anions with OAR into non-aqueous solvents is widely used for group or for more selective separations, the elimination of matrix components or the separation and preconcentration of minor or trace elements and has been reviewed in detail (112-124). Such separations have been usefully associated with radiochemical, electrochemical and spectrochemical procedures, in particular with spectrophotometry in the UV and visible regions. In early studies organic chelating agents such as enolizable 1,3-diketones, 8-hydroxyquinoline, 8-mercaptoquinoline, dithiocarbamates, monoximes or dioximes of aldehydes and ketones, hydroxamic acids, acylpyrazolones, 1,5-diphenylthiocarbazon (dithizone), N-benzoyl-N-phenylhydroxylamine, N-heterocyclic azo dyes were commonly used for the determinations of a wide range of metal ions. In addition, inner sphere (covalent) ternary complexes with a saturated coordination envelope show increased extractivity or synergistic phenomena compared with binary species (51).

Recently, charged OAR species forming ion-pairs or ion-association complexes with anions and cations became of considerable interest since ion-pair extraction is at present a most important and widely used basis for solvent extraction (125, 126). Ion-pairs may consist of anionic or cationic OAR complexes associated with tertiary amines, quaternary ammonium, arsonium or phosphonium cations, non-chelating ionized cationic or anionic dyes, voluminous anions such as tetraphenylborate or surface active macrocations or macroanions, some of them being suitable for direct spectrophotometric purposes (46, 47, 74, 127 - 130). For example extraction of various transition elements form highly absorbing anionic chelates with pyrocatechol (131, 132) or with 4-(2-pyridylazo)resorcinol (133) which may be extracted into chloroform with alkyl or phenyl arsonium and phosphonium cations respectively. The extraction spectrophotometric determination of Cu, Cd, Zn and Hg in the form of

ternary species of anionic PAR chelates with cationic surfactant in chloroform is of theoretical and practical interest (134-139). The extraction may fail in the presence of a large excess of surfactant in aqueous solution, due to micellar competition.

Some new types of OAR have recently become available for chelate-ion-pair solvent extraction. Macrocyclic crown ethers form extractable ion-pairs between the positively charged metal ion crown ether complex with some simple or complex anions, or complex zwitterions with proton dissociable crown ethers. These can be very selective extracting agents for metal ions and are now often used for the determination of alkali and alkaline earth elements. Their chemistry and analytical use including extraction have been comprehensively reviewed (140 - 147). The extraction properties and complexation are controlled by the ring size, the cavity in the structure of the reagent which is influenced by the number and position of oxygen donor atoms, by the position and nature of substituents and the stability of the ion-pairs with anions which may also be chromogenic. Thus, crown ethers containing incorporated chromophoric groups and also crown ether complex ion-pairs with selected dye anions are suitable for the sensitive extraction spectrophotometric determination of alkali and alkaline earth elements (140).

Ion-pairs of the frequently used dibenzo-18-crown-6 with picrate and containing alkali metal ions are extracted into benzene or chloroform in the order: $K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$. Thus K^+ is readily extracted for spectrophotometric determination of K^+ in the presence of excess Na^+ as an ion-pair with picrate, tropeoline OO (148), Bromocresol Green, Methyl Orange, or Metanil Yellow (149). In addition, Rb^+ , Ag^+ , Tl^+ , Pb^{2+} , NH_4^+ and alkaline earth metal ions may also be extracted into chloroform by 18-crown-6 ethers in the presence of various coloured anions (150, 151). 14-crown-4-ethers were shown to be suitable for the selective separation and spectrophotometric determination of Li^+ (152 - 154), 15-crown-5 ethers for the determination of Na^+ and 18-crown-6 ethers for the determination of K^+ and Rb^+ (155 - 157). Various monoprotion-, diproton-dissociable crown ethers and neutral crown ether dyes, in particular side-armed crown ethers with azo-linked side arms or azobenzene crown ethers have been prepared and applied in spectrophotometry (145, 158, 159). 15-crown-5-ethers with substituted azo linked side arms were recommended as chromogenic reagents for Na^+ , 4'-picrylamino-benzo-15-crown-5- or 4-picrylamino-benzo-18-crown-6-derivatives are valuable reagents for K^+ (160 - 163). Another way of using potassium complexes of crown ethers is in association with coloured anionic metal complexes and the extraction of the large ion association species into solvents of limited polarity. The extraction of $[NbOCl_2(SCN)_3]^{2-}$ or Cu^{2+} -Zincon chelate anion with the dibenzo-18-crown-6-complex of K^+ are good examples (164 - 166). Azolinked or dinitrophenylmethyl diazatetraoxa crown ethers are convenient for the spectrophotometric determination of alkaline earth metal ions, especially calcium but can be used even for sodium, after extraction into 1,2-dichloroethane (167 - 169). Macrocyclic compounds with different sizes of macrocyclic rings and different kinds and numbers of donor atoms such as O, N, S may show different extractivity and selectivity. More than 30 macrocyclic compounds have been prepared and tested for the extraction of 17 metal ions into chloroform,

in the presence of picrate as counter ion. Crown-diaza compounds and crown formazans including those with a tetraazamacrocycle selectively extract Cu^{2+} forming various types of complexes. Hg^{2+} , Pb^{2+} and Ag^+ may also be extracted at pH 5.0-5.5 with porphyrins. Macrocyclic compounds containing sulphur atoms besides oxygen extract copper, silver, mercury and palladium to variable extents (170 - 173). At present, active development of macrocyclic compounds proceeds for separation and determination of various metal ions. Heterocyclic crown ethers with mixed donor atoms have been used for the extractive determination of mercury (174). Macrocyclic Schiff bases and tetraazamacro-cycles are available for the extraction and spectrophotometric determination of copper (175-176).

Cryptands eg [2.2.2]cryptand, also show novel analytical prospects, especially for alkali metal ions, and also for Pb^{2+} (177 - 179). Na^+ was selectively extracted into chloroform in the form of ion-pairs with picrate or various dye anions and determined spectrophotometrically (180), Pb^{2+} in the presence of eosinate was determined fluorimetrically (181).

Heteropolyacids of molybdenum with phosphorus, arsenic, silicon or germanium form sparingly soluble ion association complexes with basic triphenylmethane or xanthene dye cations in acid medium which can be extracted into alkyl acetates, ketones or higher aliphatic alcohols. The reagents are often co-extracted and hence high blanks may be observed. The precipitates of such ternary species may also be floated on water-organic solvent interfaces where the solvent has low permittivity and polarity (eg xylene, hexane, cyclohexane, diisopropyl ether, toluene), washed and finally dissolved in ethanol or acetone (182 - 192). Even more complicated heteropolyacids have been used eg phosphorus or vanadium can be determined via Brilliant Green (C.I. 42040) molybdovanadophosphate after dissolution of the precipitate formed at pH 0.2-1.8 in acetone (193).

Flotation spectrophotometric procedures are also useful for the determination of various platinum metals via sparingly soluble ion-pairs of thiocyanato-complexes with rhodamine and thiazine dyes (194 - 198). In practice, although flotation procedures are especially sensitive, with conditional molar absorptivities reaching values larger than $1 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$, the variance of the results of determinations may be considerable.

A voluminous anionic complex species of a polyhedral sandwich-type, dicarbaundecaborane cobaltate(III) $([\pi-(3)-1,2-\text{B}_9\text{C}_2\text{H}_{11}]_2\text{Co}^{\text{III}})^-$, (a heteroborane anion) has recently been shown to be an excellent agent for the extraction into nitrobenzene of caesium and other alkali metal, alkaline earth metal and some other cations. (199).

Kinetic factors may sometimes be important in the extraction of metal ions with OAR species. The extraction time may differ if the reagent is dissolved in a solvent immiscible with water, or if previously added to the aqueous analyte solution in the form of a solution in a water miscible solvent (119). The extraction of chelates of some transition metal ions may be slow enough to be used as the basis of separations. Thus, Ni^{2+} can be selectively removed from other divalent metal ions

by a rate-controlled extraction separation since its azo dye chelates are extracted into chloroform much slower than those of other divalent metal ions (200). On the other hand, various types of synergistic co-extraction in systems with OAR have been explained by the formation of ternary species such as $[Ca(Sr)ScL_4]_2$ where HL corresponds with 8-hydroxyquinoline (120). For neutral OAR chelates the solvent can be regarded as a continuous structureless dielectric medium immiscible with water (119). However, for the extraction of ion-pairs the role of the organic solvent may be crucial (201). Propylene carbonate is a useful solvent being denser than water, almost odourless and of low toxicity and has been used for the extraction of a variety of ion pairs (202 - 208). Its solubility in water decreases with ionic strength but increases rapidly with temperature. This latter effect may be exploited by the formation of complexes in homogenous solution at 80°C with subsequent phase and analyte separation after cooling (208). Propylene carbonate has been shown to be a non-inert solvent in the extraction of the tetrathiocyanatocobaltate(II) anion (202). Recently solid-liquid separation after liquid-liquid extraction using molten naphthalene as extractant became popular. The equilibrium between both phases is rapidly established at the elevated temperature and the sensitivity is high due to the ease of separation of the solidified organic phase. Such techniques are useful for the extraction of complexes which are stable at higher temperatures. The precipitated naphthalene with the entrained analyte-OAR-species (chelate or ion-pair) is filtered off or separated as a pellet and dissolved in a suitable solvent (benzene, toluene, acetonitrile) and the analyte determined spectrophotometrically or by another instrumental finish (201). Useful examples are tellurium as its pyrrolidine-1-carbodithioate (209), Fe^{II} as its ternary complex with 2,2'-bipyridine and tetraphenylborate (210) and the determination of transition elements with 8-hydroxyquinoline (211). Molten 8-hydroxyquinoline is a suitable extracting medium for various of its metal complexes. The solid phase after cooling can be pulverized and pressed into pellets and the metals determined by X-ray fluorescence spectrometry (212). A convenient alternative to liquid naphthalene is the use of microcrystalline naphthalene for a solid-liquid separation (213). Other low melting point substances such as 8-hydroxyquinoline or benzophenone (214) may also be used. Microcrystalline naphthalene results from mixing a solution of naphthalene in acetone with an aqueous phase at room temperature. It shows excellent extractive-coprecipitative properties. Examples include procedures for the determination of cobalt in the form of its ternary complex with 4'-(p-methoxyphenyl)-2,2',6',2"-terpyridine or 5,6-diphenyl-3-(2-pyridyl)-1,2,4-triazine and tetrathiocyanatocobaltate(II) with Brilliant Green (216).

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