Meetings

Metal Chelates in Analytical Chemistry

Chelating agents are of great use in analyzing metals. Ligands which form charged metal chelates are used in titrimetry, as masking agents, or in separations based on the ion-exchange principle. Ligands which form uncharged metal chelates are used as the basis of analytical separations such as precipitation, solvent extraction, and chromatography, including gas-phase chromatography for volatile chelates.

At the 16th Annual Analytical Symposium held at the University of Arizona on 19–21 June 1963 various aspects of the role of metal chelates in analytical chemistry were discussed. [A more detailed report can be found in *Anal. Chem.* **35**, 1994 (1963).]

Charles N. Reilley (University of North Carolina) discussed the theory of metal titrations with EDTA, emphasizing the role of kinetics of chelate formation and dissociation as well as the equilibrium aspects in such reactions. A reasonable prediction of the feasibility of many end-point reactions can be made by considering the nature of the molecular structure of both the chelating titrant and the metallochromic indicator. The rate of reaction of the metal-indicator complex with the titrant becomes slower as the number of metal coordination sites in the indicator molecule decreases.

Variation in the parts of the structure of the indicator, other than the chelation sites, can significantly influence the rate of end-point reactions. Substituents that withdraw electrons or that offer steric hindrance to chelation increase lability as well as reduce stability. Steric effects influence the role of the structure of the titrant and the end-point reaction rates. The nature of the metal ion being titrated also plays a part in the rate of the end-point reaction. In general, the smaller the ionic radius and the larger the charge on the metal ion, it is more likely that its end-point reaction will be slow.

Concerning back titrations, success often depends on not reaching one or more equilibriums; here the basic problem is the reduction of the rate at which these undesirable equilibriums are attained.

Nuclear magnetic resonance techniques are useful in the study of the structure, solution equilibriums, and even reaction kinetics of metal chelates. From such measurements, the acid dissociation constants and protonation sites of chelating titrants can often be determined. By observing the *p*H dependency of certain proton chemical shifts in solutions containing the ligand and the nonparamagnetic metal ion, metal-chelate formation constants may be determined.

H. Flaschka (Georgia Tech) discussed the application of photometric titration as a means of increasing the sensitivity of chelometric titrations. In contrast to *p*H or other potentiometric titrations, photometric titrations are linear in that the quantity measured as the titration proceeds is directly proportional to the concentration, rather than being logarithmically related. The shapes of such titration curves consist of two-line segments easily extrapolated to meet at the end point, rather than the sigmoid shape associated with logarithmic titration curves. The sharpness of the end point in such a titration is much more dependent on the magnitude of the equilibrium constant of the titration reaction than is that of the linear titration where straight line segments are obtained in the presence of a large excess of one of the reactants.

There are two general types of photometric indicators. First, the step indicator is one which is added in a very small amount and changes color at the end point resulting in a step-shaped titration curve. Second, the term "slope" of "self" indicator is applied when any of the species involved in the titration absorbs. Titration curves of self-indicating systems show only one change of slope which is less abrupt than the slope changes seen for step indicators. Self-indicating systems can be used in place of metallochromic indicators for nonindicating systems, thereby eliminating some of the problems associated with these dyes. Greater selectivity can be achieved with "slope" than with "step" indicators. For example, when calcium and magnesium are titrated with EDTA in the usual fashion, the sum of calcium and magnesium is obtained. If, however, the Erio T is added in excess of the amount of magnesium present, then a slope titration results in which the magnesium indicator complex acts as a self-indicator. The final result is that the two slope changes in the titration curve permit the analysis of calcium and magnesium in each other's presence and Flaschka developed a method for determining both calcium and magnesium in a single drop of blood serum. Methods were described for determining cadmium and zinc in the presence of one another in an ammoniacal solution with copper as a slope indicator and EGTA [ethylene glycolbis-(β-aminoethyl ether)-*N,N,N′,N′*, tetraacetic acid] as titrant.

Robert L. Pecsok (University of California, Los Angeles) discussed the effects of chelation on electrochemical behavior, and, conversely, the interpretation of such behavior to elucidate the nature and properties of metal chelates. The formation constant of the Cr(II)-EDTA complex was evaluated for the first time by the potentiometric technique modified to obviate the difficulty imposed by the rapid oxidation of Cr(II).

The $CrY^{=}$ was shown to protonate to form $CrHY^{-}$. From the similarity of the pK_a of this species to those of analogous species with other divalent transition metal ions, it was concluded that $CrY^{=}$ has a quinquedentate structure.

The $CrY^{=}$ was shown to have a d^4 configuration with four unpaired electrons from magnetic susceptibility measurements. From polarographic experiments, the value of the formation constant of CrY^{-} was calculated as log $K_f = 23.40$.

G. J. Abel, Jr. (American Smelting and Refinery Central Research Laboratories) discussed the application of EDTA to the analysis of nonferrous materials indicating that EDTA procedures were used for the analysis of one or more elements in virtually every alloy produced as well as in the many raw materials and by-products associated with the nonferrous industry.

Lead is one of the basic elements which is determined in brass, bronze, solder, white metals, drosses, and ores after separation as lead sulfate. Tin, antimony, and arsenic are removed by hydrobromic acid–bromine volatilization and the precipitated lead sulfate is separated by filtration, dissolved and titrated with EDTA and Eriochrome Black T. Zinc is determined in brass, bronze, diecast, slush metal, silver solders, and by-products by EDTA titration, with Eriochrome Black T as indictor. Zinc in aluminum-base alloys may be separated by passing a solution $0.75M$ in hydrochloric acid through a column of Dowex 1. The adsorbed zinc is eluted with water and titrated. Nickel, aluminum, and magnesium are also determined by an EDTA titration. Details of the analysis of fusible alloys containing bismuth, lead, cadmium, indium, and tin which were an analyst's nightmare before the advent of EDTA were also described by Abel.

R. Belcher (University of Birmingham, England) described a study of the reactions of silver with *p*-dimethylaminobenzalrhodanine and over 30 other similar organic compounds which were synthesized. From the work done so far, the complexing process appears to be less simple than was first supposed; moreover, the silver reaction can take place even though the imino hydrogen is absent.

The discovery of EDTA as a titrant led to extensive investigations to find new indicators. This in turn led to the further examination of these indicators as spectrophotometric reagents. As a consequence of these investigations, alizarin complexone was found by Belcher and his co-workers to give a stable chelate with cerium (III) ions, which further formed a 1 : 1 : 1 complex with fluoride.

The dyestuff Fast Sulphon Black F was first studied as an EDTA indicator for copper because its highly selective reaction suggested that it might have useful properties as a spectrophotometric reagent for determining copper. It was found that the only metal whose interference could not be masked was beryllium since its color persists in the presence of cyanide. Accordingly, this provided a specific colorimetric reaction for beryllium.

Another reagent which was first synthesized as an indicator for the titration of calcium with EDTA was obtained by diazotizing H-acid. This compound is very advantageous as a spectrophotometric reagent for determining calcium. The compound 4-(2-pyridylazo) resorcinol has been studied by various investigators as a spectrophotometric reagent. Conditions have now been established in which only niobium reacts specifically in the presence of most other metals including tantalum. The compound bromopyrogallol red is a valuable spectrophotometric reagent for determining niobium and silver; its sensitivity is enhanced by the formation of a ternary complex.

Investigations of *o,o′*-dihydroxyazo compounds by Diehl and his co-workers at Iowa State University uncovered an azo dye that gave a color with magnesium but not with calcium. The magnesium compound proved fluorescent and provided a basis for both a fluorometric and colorimetric method for magnesium. The methods have been applied successfully to the determination of magnesium in water, serum, limestone, iron ore, and cement.

The usefulness of the *vic*-dioximes as selective analytical reagents has been steadily increasing since they were first proposed for this purpose in 1905 by Tschugaeff. The *vic*-dioximes available today are widely used for separations involving precipitations and extractions. These reagents are also extensively used for the gravimetric, titrimetric, and spectrophotometric determination of various metals. These reagents are commonly used for the gravimetric determination of nickel and palladium. The *vic*-dioximes have also been used as the basis for alkalimetric, oxidimetric, complexometric, amperometric, non aqueous, and heterometric methods of analysis. Rhenium, iron, nickel, cobalt, and copper are among the metals that can be determined spectrophotometrically with the *vic*-dioximes. The isomerization, crystal structure, nomenclature, and the analytical applications of the *vic*-dioximes were discussed by Charles V. Banks (Iowa State University).

The chemical, magnetic susceptibility, infrared, x-ray diffraction, and thermodynamic evidence concerning the structure of the insoluble metal-(II)-*vic*-dioxime coordination compounds were reveiwed. The crystal structures were correlated with such properties as solubility product constant, intrinsic solubility, overall stability constant, and absorption spectra showing the way to new and improved *vic*-dioximes for specific analytical applications.

8-Mercaptoquinoline, a hygroscopic blue liquid which forms a crystalline red dihydrate, was introduced first in 1944 by Taylor who stated that it could not be a useful analytical reagent because of ready oxidation to the bis-8-quinolyldisulfide. Freiser and co-workers (University of Arizona) found, that with reasonable precautions, however, the oxidation can be largely eliminated. Not until recently has 8-mercaptoquinoline received much attention in analytical applications

Since 8-mercaptoquinoline would appear to have potentialities as useful and as versatile as 8-hydroxyquinoline, a study of the formation constants of metal chelates of 8-mercaptoquinoline was undertaken. Although 8-mercaptoquinoline is significantly more acidic than 8-hydroxyquinoline, its chelates are as stable (similar K_f values) and form at lower *p*H values (higher proton exchange constants) than the 8-hydroxyquinoline chelates. The analytical significance of these results was discussed.

Complexes between soluble polyelectrolytes and metal ions are well known; and their formation constants may be calculated accurately from direct acid-base titration curves, provided that suitable functions are employed. This was demonstrated by H. P. Gregor and co-workers (Polytechnic Institute of Brooklyn), using both titration and dialysis techniques.

In forming complexes with metal ions, water soluble polyelectrolytes are often cross-linked to form insoluble gels. Gel formation was studied quantitatively by light-scattering techniques. These gels can be redissolved by the addition of a suitable concentration of low molecular weight ligand of appropriate binding power. As a result, mixed polyelectrolyte metal complexes are formed. The equilibrium constants for this formation process can be determined by using the equilibrium dialysis technique because the polyelectrolyte and its complexes are nondiffusible.

Gregor also described an equilibrium study concerning the properties of a typical metal-polyelectrolyte system and their utility in analytical chemistry. The polymer employed was (100,000 molecular weight) poly-*N*-vinylimidazole (P-VI), a commercially available material having certain properties analogous to those of many biopolymers. Among other things this polymer shows a maximum coordination number of 4 with Zn(II) and Cu(II). Formation constants were calculated from data obtained in the presence of a high con-

centration of neutral salt and at a high equivalence ratio of polymer to metal ion. The successive binding constants for the zinc-polyvinylimidazole system increased as the number of ligands attached to the metal ions increased. The stoichiometry of PVI-Zn complexes was studied by precipitating the polymer in the presence of different ratios of polymer to zinc.

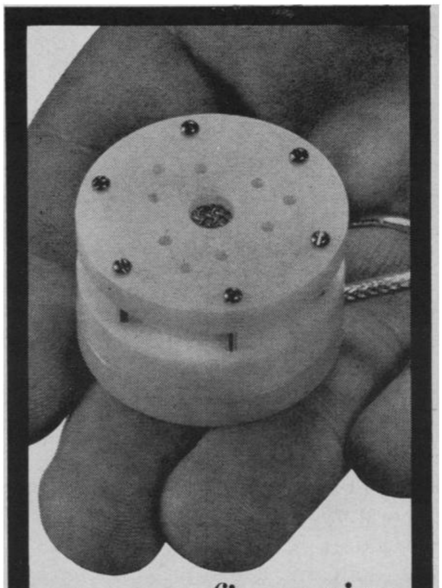
The turbidity of PVI-Zn complexes, studied by light scattering, increased as polymer was added at a constant metal ion concentration; at higher polymer concentrations the turbidity decreased. When an excess of metal ion was present, it acted as a cross-linking agent and high molecular weights were obtained, ones which decreased as more polymer was added to the system with a resultant shift to intramolecular as opposed to intermolecular cross-linking.

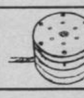
The theory of the solvent extraction of metal chelates was developed in considerable detail by both David Dryssen (Royal Institute of Technology, Sweden) and George Schweitzer (University of Tennessee). Equations for the various equilibriums were developed, and methods for identifying the dominant organic and aqueous species were described. From these relationships, various means of controlling extractions were discussed.

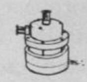
A comparison of some extraction constants or pH_{50} values with the constants for the first steps in the mononuclear hydrolysis of the metal ion was made. Dryssen noted that as the extraction constant of a reagent decreased, the spread of pH_{50} (pH at which 50 percent metal is extracted) values of the metals increased. Effects of the metal ion concentration such as polynuclear hydrolysis, precipitation of the metal chelate, and radiocolloid formation were discussed.

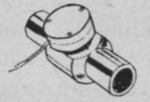
The formation of adducts in the organic phase with the uncharged extractable metal chelate, MA_N, and some mixed solvent effects were treated; the extraction of mixed chelates and some practical applications of mixed chelate extraction were discussed.

Chelate extractions with TTA (1,1,1,-trifluoro-3,2-thenoylacetone) were reviewed by Oscar Menis (Nuclear Materials and Equipment Corporation). Parameters, including pH, solvent, and aqueous environment, were evaluated in terms of their enhancing, complexing, and kinetic effects. A general term, "synergistic effect," describes the influence of two or more factors on the magnitude of the distribution ratio of a









metal complex. A comparison was given of the various mechanisms for agents which when combined produce a greater effect than when each acts individually (such as adduct formation, solvent coordination, and mixed chelate formation). In addition, the utilization of the competitive action of complex ligands forming complexes in aqueous media for separating groups of metal chelates was discussed.

Philip W. West (Louisiana State University) discussed the application of agents that induce complex formation for the development of greater selectivity in metal separations and determinations by masking interfering metal ions.

The usefulness of metal chelates in chemical separations of radioactive substances was amply demonstrated by H. L. Finston (Brookhaven National Laboratory). Rapid solvent extraction procedures necessary for the isolation and study of short-lived radionuclides were pointed out. Decontamination factors of greater than 10^{12} have been obtained in the separation of uranium from associated fission products after neutron irradiation, by extraction with dibenzoylmethane in the presence of DCTA.

R. L. Sievers (Wright-Patterson Air Force Base) discussed volatile metal chelates in the separation and analysis of metals by gas-phase chromatography. Metal chelates of acetylacetone, trifluoroacetylacetone, and hexafluoroacetylacetone were studied. A number of chelates can be eluted at column temperatures far below their boiling points and in most cases below or near their melting points. A definite trend was observed in the relative ease of elution. Chelates of the fluorine-containing β-diketones are considerably more volatile and can be eluted at much lower column temperatures than corresponding complexes of acetylacetone. Column temperatures as low as 30°C have been used in separations of hexafluoroacetylacetonate complexes.

Trifluoroacetylacetonate chelates of beryllium(II), aluminum(III), gallium(III), indium(III), chromium(III), iron(III) copper(II), rhodium(III), zirconium(IV), and hafnium(IV) have been eluted successfully. Separations of several mixtures of these complexes have been achieved.

The fluorine-containing chelates can be detected by electron capture even when the quantities of halogen-containing organic compounds are of the order of 10^{-12} grams. Gas chromatography was used to separate *cis* and *trans*

isomers and optical isomers of metal chelates. Optical isomers were separated on columns which contained optically active stationary phases.

J. Coleman (Harvard Medical School) discussed his work with B. Vallee on the inhibition of metalloenzymes by chelating agents. The role of the metal was described as that of a reactive group of the enzyme molecule involved in activity which is lost when the metal atom is either removed or interacts with chelating agents to form a mixed complex.

The banquet speaker, G. Kuiper (Lunar and Planetary Laboratory, University of Arizona), discussed the composition of planetary atmospheres. Specialized techniques of high-resolution absorption spectroscopy including matching of spectra of laboratory-developed gaseous systems with those observed by telescope have been ingeniously used to obtain rather detailed information on atmospheres of a number of planets.

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Forthcoming Events

February

2–5. American Inst. of **Chemical Engineers**, annual, Boston, Mass. (J. Henry, AICE, 345 E. 47 St., New York, N.Y.)

2–7. Institute of **Electrical and Electronics Engineers**, winter meeting, New York, N.Y. (A. P. Fughill, Detroit Edison Co., 2000 Second Ave., Detroit, Mich. 48226)

2–8. **Teratology**, workshop, Commission on Drug Safety, Gainesville, Fla. (D. C. Trexler, Commission on Drug Safety, 221 N. LaSalle St., Chicago, Ill. 60601)

2–11. Scientific-Technical **Documentation and Information**, intern. congr., Rome, Italy. (I. M. Lombardo, La Produttivita, Viale Regina Margherita, 84d, Rome)

3–4. Society of **Rheology**, Claremont, Calif. (T. L. Smith, Stanford Research Inst., Menlo Park, Calif.)

3–4. Perspectives in **Virology** IV, Gustav Stern symp., New York, N.Y. (M. Pollard, Lobund Laboratory, Univ. of Notre Dame, Notre Dame, Ind.)

3–7. **Materials**, intern. conf., Philadelphia, Pa. (A. G. H. Dietz, Dept. of Building Engineering, Massachusetts Inst. of Technology, Cambridge)

4–6. Society of the **Plastics** Industry, conf. of the reinforced plastics div., Chicago, Ill. (W. C. Bird, SPI, 250 Park Ave., New York, N.Y. 10017)

4–6. Cellular Biology of **Myxovirus Infections**, CIBA Foundation symp., London, England. (CIBA Foundation, 41 Portland Pl., London, W.1)

5–7. **Military Electronics**, 1964 winter conv., Los Angeles, Calif. (Inst. of Electrical and Electronics Engineers, Box A, Lenox Hill Station, New York, N.Y.)

5–8. American College of **Radiology**, natl. meeting, Tucson, Ariz. (American College of Radiology, 20 N. Wacker Dr., Chicago, Ill. 60606)

7–8. **Differentiation and Development**, symp., New York, N.Y. (New York Heart Assoc., 10 Columbus Circle, New York, N.Y. 10019)

9–11. **Entomological** Soc. of America, Southwestern Branch, Monterrey, Mex. (D. F. Martin, P.O. Box 1033, Brownsville, Tex. 78521)

10–14. New Zealand Institution of **Engineers**, conf., Wellington. (F. N. Stace, P.O. Box 3047, Wellington, N.Z.)

12–16. American College of **Cardiology**, 13th annual, New Orleans, La. (P. Reichert, Empire State Bldg., New York, N.Y. 10001)

13–14. Texas **Industrial Pharmacy** Seminar, Austin. (L. R. Parker, Pharmacy Extension Service, Univ. of Texas, Austin)

15–16. **Atomic Energy**, Japanese natl. symp., Tokyo. (Atomic Energy Soc. of Japan c/o Atomic Energy Research Inst., 1-1 Shiba-tamura-cho, Minato-ku, Tokyo)

16–22. **National Engineers'** Week, sponsored by the National Society of Professional Engineers. (2029 K St., NW, Washington, D.C. 20006)

17–19. American **Standards Assoc.**, 14th annual conf., Washington, D.C. (ASA, 10 E. 40 St., New York, N.Y. 10016)

17–20. **Metals** for Use at High Temperature, intern. symp., New York, N.Y. (D. A. Parks, Inst. of Metals Div., Metallurgical Soc., 345 E. 47 St., New York, N.Y. 10017)

17–21. **Information** Storage and Retrieval, 6th, Washington, D.C. (L. W. Hattery, American Univ., 1901 F St., NW, Washington, D.C. 20006)

19–21. National Soc. of **College Teachers** of Education, Chicago, Ill. (E. J. Clark, Indiana State College, Terre Haute, Ind.)

19–21. **Solid-State Circuits**, intern. conf., Philadelphia, Pa. (L. Winner, 152 W. 42 St., New York, N.Y. 10036)

19–22. American **Educational Research** Assoc., Chicago, Ill. (J. R. Gerberich, 1201 16th St., NW, Washington, D.C.)

19–5. Pan American **Medical** Assoc., 39th congr., the Americas, during a cruise aboard the S.S. *Independence.* (J. J. Eller, 745 Fifth Ave., New York, N.Y.)

23–27. Technical Assoc. of the **Pulp and Paper** Industry, 49th annual, New York, N.Y. (TAPPI, 360 Lexington Ave., New York, N.Y. 10017)

23–28. **Otorhinolaryngology and Bronchoesophagology**, 9th Pan American congr., Bogota, Colombia. (C. M. Norris, 3401 N. Broad St., Philadelphia, Pa.)

24–25. Atmospheric Movements of **Radioactive Materials**, Geneva, Switzerland. (World Meteorological Organization, Geneva)

24–25. **Writing-Improvement** Programs for Engineers, seminar, New York, N.Y. (C. A. Meyer, RCA Commercial Engineering, Harrison, N.J.)