FINAL PROGRESS REPORT

ANALYTICAL METHODOLOGY FOR ENVIRONMENTAL MEASUREMENTS

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ABSTRACT

The scientific accomplishments achieved by the principal investigator and his co-workers during the 22 year period of this contract and its predecessors are summarized. Reference is made to 94 scientific papers resulting from the work and a list of 38 students receiving Ph.D. degrees while supported by the contracts is given.

SCIENTIFIC ACCOMPLISHMENTS UNDER THE CONTRACT

When the parent contract, AT(30-1)-905, between the United States Atomic Energy Commission and the Massachusetts Institute of Technology was signed on June 19, 1950, it brought together under Commission sponsorship three discipline-related research groups previously funded by the Office of Naval Research. These were entitled Inorganic Nuclear Chemistry, Chemistry of the Fission Elements, and Radioactive Tracer Studies of Organic Chemistry, under the direction of Professors Charles D. Coryell, David N. Hume and John D. Roberts, respectively. These groups, with the addition of Physical Chemistry under Professor George Scatchard enjoyed a long, congenial and productive association together, mostly within the administrative structure of the M. I. T. Laboratory for Nuclear Science. Now, following the death, retirement or transfer of the other senior principal investigators and the phasing out of various areas of chemical activity by the Commission, the last remaining group currently listed as AT(11-1)-2169, is being transferred to the National Science Foundation. The present document represents therefore, the terminal report of this undertaking.

The Chemistry of the Fission Elements group, in accordance with the language of the parent contract, was not limited to the specific

subjects enumerated in that document, namely fundamental studies of the rarer elements, fundamental studies on the electroseparation of carrier free traces, studies of methods suitable for quantitative determination of submicrogram quantities of materials, fundamental studies of polarography including practical applications to the fission elements, and development of improved methods of measuring radioactivity. Numerous investigations in related areas were carried out and, over the years, a number of co-senior investigators have taken part: notable among these being Professors L. B. Rogers, J. W. Ross, D. K. Roe and D. M. Hercules. The present report attempts only to survey and summarize that portion of the whole effort which was directed and supervised by the writer. Over the period of the contract, 35 students received MIT-granted Ph.D. degrees based on this work, 3 were granted External Ph.D. degrees by foreign universities, and 3 S.M. degrees by M.I. T. Seven postdoctoral research associates were involved in the work and about a dozen undergraduate students participated. A list of those receiving degrees is appended to the report. Ninety scientific publications have appeared in the chemical literature as a direct consequence of the work and four more are in press. A bibliography of publications is appended.

A glance at the bibliography makes clear that the work of the

project covered a wide range of rather diverse topics. Most of it, however, can be characterized either as the development of new analytical techniques and methodology or demonstration of the application of these to chemical problems of intrinsic interest. Many of the applications have been in the areas of complex ion chemistry, trace analysis and, particularly recently, environmental trace metal studies. The following summary is an effort to provide an orderly account of the work accomplished and a topical guide to the chronological list of published accomplishments.

One of the principal work categories has been studies of complex ion chemistry, largely by instrumental analytical techniques. A number of fundamental investigations have been made which have led to new methods for the identification of complex ion compositions and the measurement of complex ion stability constants, particularly consecutive constants in series of complexes formed by stepwise addition or replacement. In particular, the spectrophotometric method of Newman and Hume (31) and the polarographic method of De Ford and Hume (4) for measuring consecutive stability constants have attracted attention and been utilized by many other workers. Significant contributions to the solubility method of measuring consecutive stability constants have been made by Cave and Hume (14)

and Burns and Hume (23). The work of Heintz and Hume (29) which was a careful examination of the validity of the interfacial tension method for studying complexes, put an abrupt end to a long series of papers coming from another laboratory. The measurement of stability constants in mixed ligand systems is a particularly difficult task and the work of Newman and Hume (33) provided a workable means of utilizing spectrophotometric data for this purpose. The evaluation of computer techniques in this area has been discussed by Hume (89).

A considerable number of systems have been studied by the methods devised or refined in this laboratory. Chemical characteristics, usually including stability constants, have been studied spectrophotometrically for the systems lead and nitrate (10) indium and bromide (30), bismuth and chloride (32), bismuth and bromide (33), bismuth and iodide (64, 77) copper bromide (55, 58), nickel bromide (91), nickel cyanide (67) and transition metals with hexamethylene tetramine (86). The mixed ligand systems, bismuth with chloride and bromide (33), mercury with halides (52) (56) lead with chloride and bromide (59) and mercuric cyanide with chloride, bromide and thiocyanate were found amenable to spectrophotometric analysis.

The polarographic method has been applied with success to

measurement of stepwise stability constants in the following systems: cadmium and thiocyanate (5), lead and nitrate (10), zinc and thiocyanate (12) lead and acetate (23), lead and thallium with thiocyanate (25), mercury and cyanide (35), lead in cyanide medium (38), mercury, hydroxide and cyanide (42), lead and fluoride (58) and copper, cadmium and zinc with fluoride (60). Solubility methods were used in the study of the silver and thiocyanate (14), lead and acetate (23), lead and fluoride (58), lead and hydroxide (72) and mercury oxycyanide (42) systems. Liquid-liquid extraction methods with computer-calculation were used with the hafnium and fluoride systems (54, 61). Potentiometric techniques were used as an adjunct in a number of the above studies but particular mention should be made of the fluoroborate system in which two specific ion electrodes were used simultaneously to get the necessary data for calculation of the constants of the mixed ligand (fluoride and hydroxide) equilibria involved (90).

A second major work category in this project has been the development of new and improved analytical techniques and methodologies. Two of the most important of these were novel instrumental titration methods based on light absorption and temperature changes respectively. The fundamental theory of photometric titration was first worked out by Goddu and Hume (15) with particular reference to

the measurement of weak acids. Among the applications demonstrated was the determination of weak acids in aqueous media (16), the determination of vanadium at trace levels, (2), cerium (26), weak acids in non-aqueous media (48), weak bases in non-aqueous media (46), and automatic photometric titration. The photometric titration technique has proved to have considerable practical value in industry and is now sufficiently widely used to justify the publication of a book on the subject.

Automatic thermometric titration was first demonstrated by Linde, Rogers and Hume (11) and has likewise been found important enough in practical analysis and research to call for the marketing of a commercial titrator and the publication of two monographs on its theory and applications.

In this laboratory, fundamental work has been done on the theory of thermometric titration curves (22) and in titrations in nonaqueous solvents, notably acetonitrile (65), and glacial acetic acid (66). The advantages of the technique in measurement of heats of reaction has been pointed out (22) and demonstrated in studies on the heats of neutralization of amines in acetonitrile (39). Most recently, the technique of thermometric titration with gaseous reagents has been demonstrated (88).

Electrochemical methods, principally polarography and its variants, have been represented by apparatus development (6, 61), fundamental studies on the mercury coated graphite electrode (92), the development of techniques for polarography in high temperature molten salt systems (51), coulometric titration based on electro-generation of sulfhydryl compounds (43) and thioethyleglycol (47), and the measurement of transference numbers in concentrated sodium perchlorate solutions (70). For a number of years, biennial critical surveys of the literature covering polarographic theory instrumentation and methodology were published in Analytical Chemistry (20, 34, 45, 53, 71, 75, 82). A precise low-level polarographic method for the determination of silver (7) and an amperometric titration for cerium (38) were developed.

In the area of spectrochemical emission, fundamental studies were made of factors affecting emission intensities and mutual cation interference effects in flame photometry (40, 41). Matrix effects in the flame photometric determination of barium and strontium (76) were studied as background for the development of a method for the determination of strontium and barium at natural levels in sea water (80). The technique of emission spectroscopy using a radiofrequency generated plasma coupled with an ultrasonic atomizer system was developed and demonstrated (63) and a modification later applied with

considerable success to the determination of mercury at part per billion levels in environmental water systems (87). Absorption spectrophotometry has been used as the basis of a number of sensitive new analytical methods: the determination of niobium (8), silver (9), niobium in the presence of tantalum (17), manganese (18), fluoride (81), aliphatic amines (27), and cerium in a combined photometric-radiometric procedure (1), which stimulated the development of a new technique of counting for liquid samples (3).

A number of the investigations carried out in the course of the work do not fit into main categories. Among these should be mentioned studies on the measurement of relaxation times in nuclear magnetic resonance (73, 74), a NMR study of the alleged formation of hexacyanonickelate in aqueous solution (67), fundamental examination of acid base equilibria in low dielectric-constant solvents (49), a study of ion-exchange equilibria in liquid ammonia (79), the preparation of water- and hydroxide-free chloride melts (44), methods of preparing low temperature baths (84), the determination of amides (62), and a rapid molten-salt method for dissolving platinum metals (68). Environmentally related studies have assumed an increasing importance in the work of the group, and it might be worth pointing out that this began long before environmental involvement became

fashionable, the first work beginning in 1963 and publications starting to appear in 1966 (76). Besides the work already mentioned on methods for the determination of barium and strontium in sea water (76, 80), the determination of mercury in environmental water (87), and the use of the mercury coated graphite electrode for the study of trace metals in environmental water (92), there has been work on the measurement of barium and strontium as a function of location and depth at sea (83).

Work initiated under the present contract and either near completion but not yet published, or being continued under NSF auspices includes development and demonstration of methods for determination of copper, lead, cadmium, silver, bismuth and antimony in sea water by means of anodic stripping voltammetry, improved cold vapor atomic absorption methods for determination of mercury in organomercurial compounds and organic matrices, the development and demonstration of electrochemical sensors for measurement of sulfur dioxide and carbon monoxide in air, the detection and determination of nitrilotriacetic acid in environmental water systems in the p.p.b. range, and studies of processes taking place in the radio-frequency plasma emission source.

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STUDENTS GRANTED Ph. D. DEGREES
SUPPORTED BY THE CONTRACTS

1. Norman F. LeBlanc (1950)
2. G. C. B. Cave (1951)
3. Robert G. Goddu (1951)
4. Herbert M. Hershenson (1952)
5. Kenneth W. Gardiner (1952)
6. Charles Merritt (1953)
7. Michael A. DeSesa (1953)
8. Thomas L. Marple (1954)
9. Richard P. Buck (1954)
10. William C. Purdy (1955)
11. Edwin R. Leder (1955)
12. Eugene A. Burns (1956)
13. Hubert J. Keily (1956)
14. Leonard Newman (1957)
15. Earl J. Forman (1957)
16. Walter H. Foster (1959)
17. L. E. I. Hummelstedt (1959)
18. Barry Miller (1959)
19. Donald L. Maricle (1959)
20. Thomas G. Spiro (1960)
21. Leland W. Marple (1960)
22. Betty S. Duffield (1960)
23. David R. Gabbe (1962)
24. Richard A. Durst (1963)
25. Stefica S. Mesarić (1964)

26. Adrian J. Eve (1964)
27. Alan M. Phipps (1964)
28. Charles D. West (1964)
29. Neil R. Andersen (1965)
30. James N. Little (1966)
31. Adrienne S. Gordon (1966)
32. Theodore J. Retajczyk (1966)
33. William Boardman (1967)
34. Arthur L. Malenfant (1967)
35. William F. Fitzgerald (1969)
36. Donald Shive (1969)
37. W. Rudolf Seitz (1970)
38. Thomas R. Gilbert (1971)

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