ENGINEERING RESEARCH INSTITUTE
UNIVERSITY OF MICHIGAN
ANN ARBOR

FINAL REPORT

CONTROL INDICES AND ANALYTICAL PROCEDURES

By

PHILIP J. ELVING

Project 2121-1

U.S. ATOMIC ENERGY COMMISSION
CONTRACT NO. AT(10-1)-733

February, 1954

Engle
UHR
1147

SUMMARY

In this final report on Project 2121-1, Control Indices and Analytical Procedures, of Contract No. AT(10-1)-733, the basis for the specific investigations which were undertaken during the course of the project is indicated and the accomplishments of the project are listed in the principal project outline submitted by the sponsoring agency.

The fifteen research reports issued as a result of the project work, by which the results have been communicated to the sponsoring agency, are also listed.

FINAL REPORT

CONTROL INDICES AND ANALYTICAL PROCEDURES

The present report, being the final one on Project 2121-1, is an attempt to indicate why the work was done, what was accomplished, and where the results of the work can be found. Consequently, the report is divided into three sections. The first section is a detailed list of the authorizations, requests, and discussions which formed the basis for the investigations and studies undertaken on the project. In the second section the results of the project work are presented in the form of an annotated outline which is based on the principal statement of the aims of the project as formulated by the sponsoring agency. The third section consists of a list of the fifteen research reports issued as a result of the project work; these reports constitute the most tangible result of the work, since they are the form in which the information obtained and the methods and procedures developed have been communicated to the sponsoring agency.

It is a pleasure to list here the names of those who have worked on the project at various times during the past year and who by their efforts have produced whatever results are of value: Victor Bloom, Anna Griffin, Philomena Grodzka, Edward C. Olson, Bernard Zemel, and Martha B. Wells.

A. BASIS FOR SPECIFIC INVESTIGATIONS

The specific research and development projects which were undertaken were based on the outlines, requests, and suggestions set forth in the following principal statements and correspondence concerning the work:

(1) Letter of F. A. Hall of the American Cyanamid Company to George G. Brown, Dean of the University of Michigan College of Engineering, dated November 6, 1952, with accompanying description of the investigations desired.

(2) Outline of investigations to be undertaken, specifying $7220 and $9600 as the costs, respectively, of the control index studies and analytical procedure development.

(3) Preliminary draft of item (4).

(4) Detailed description of investigations desired, setting forth the division of the work to be followed, and entitled "Development Projects, University of Michigan, February 18, 1953." This material consists of three sections under "Analytical Procedure Studies" and three sections under "Control Index Studies", and represents the principal basis for the studies.

(5) Verbal discussion on occasion of visit of P. J. Elving to Idaho Falls on May 28 and 29, 1953. In this connection, see item (6).

(6) Memo from R. J. Francel of the American Cyanamid Company to F. L. Steahly of the American Cyanamid Company, dated June 6, 1953, and numbered CPP-602, embodying the results of the discussion indicated in item (5). This memo had major effect in modifying the requirements of item (4) by setting up more difficult objectives.

(7) Letter from G. C. Voss of the American Cyanamid Company to P. J. Elving, dated August 14, 1953, expressing the opinions of American Cyanamid analytical chemists on the status of the work being done at Michigan.

(8) Letter from P. J. Elving to H. B. Coates of the Blaw-Knox Company, dated October 9, 1953, and prepared as a result of Dr. Coates' visit to Ann Arbor on behalf of the Atomic Energy Commission to evaluate the work of the project at Michigan.

(9) Conference at Ann Arbor on November 18, 1953, between W. L. Ginkel of the Atomic Energy Commission and P. J. Elving, in which certain changes in the direction of the work were suggested.

(10) Letter from J. B. Philipson of the Atomic Energy Commission to P. J. Elving, dated December 23, 1953, confirming the conversation of item (9) and requesting further changes and, if possible, further investigations.

B. SUMMARY OF ACCOMPLISHMENTS

Essentially all the work requested was done except that some groups of data are less complete than desired. There was a considerable

amount of wasted effort on the project due to a number of factors, among which were the misunderstandings and delays resulting from the change in operating companies and in supervisors of the project in Idaho. A large amount of time and energy was needlessly expended as a result of the submittal of incorrect samples of stainless steel; some additional time was lost due to poor zirconium samples. However, all factors considered, it is believed that some satisfactory work has been done; e.g., the chemists at Idaho have been enthusiastic about the procedure for the analytical determination of zirconium in fluoride solution (Progress Reports Nos. 4 and 7). This method has apparently resolved certain long-standing analytical difficulties.

The specific accomplishments of the project are indicated in the following outline, which is based on the principal statement of the investigations desired which is described as item (4) under "A. Basis for Specific Investigations."

Analytical Procedure Studies

I. Determination of Analytical Procedures for Zirconium and Fluoride in Zirconium Fluoride - Hydrofluoric Acid Solutions, and II. Determination of Analytical Procedure for Zirconium, Aluminum, and Fluoride in a Mixed Inorganic Salt Solution. Progress Report No. 4 presents an analytical method for zirconium based on amperometric titration with cupferron. Progress Report No. 5 describes the spectrophotometric determination of aluminum as the 8-hydroxyquinolate. Progress Report No. 6 covers the indirect polarographic determination of fluoride. These methods were developed with careful attention to the use to which they were to be put and the conditions under which they were to be used. The precision and accuracy are in all cases considerably better than those which were requested.

Progress Report No. 7 presents specific analytical procedures, based on Progress Reports Nos. 4, 5, and 6, for analyzing the two types of solutions specified in the work plans.

Progress Report No. 14 describes the application of the procedures of Progress Reports Nos. 4, 5, and 6 to the two types of solutions specified when small amounts of tin or uranium are present.

III. Determination of Analytical Procedures for Iron, Chromium, Sulfate, and Nitrate in a Mixed Inorganic Salt Solution. Progress Report No. 12 describes an analytical method for sulfate based on amperometric titration with lead ion solution. Progress Report No. 13 presents a photometric procedure for the determination of nitrate. Progress Report No. 15

describes a polarographic method for the determination of chromium and a second polarographic method for the simultaneous determination of chromium and iron. These methods, which were developed from methods described in the literature were adapted to the specific type of solution and to the specific conditions of measurement concerned. The precision and accuracy were in all cases satisfactory.

Progress Report No. 16 presents specific analytical procedures, based on Progress Reports Nos. 12, 13, and 15, for analyzing the type of solution specified in the work plans.

Control Index Studies

I. Determination of the Relationship of Specific Gravity to Zirconium Concentration. Progress Report No. 3 deals with the relation at 25°C between the density of hydrofluoric acid solutions and their hydrogen fluoride concentration in terms of molarity and of percentage by weight for the range of 5-9M hydrofluoric acid in which we are interested. This work was done because available tables of data were found to be in error.

Progress Report No. 8 is an account of the density measurements made at three temperatures on zirconium fluoride - hydrofluoric acid solutions in which the initial concentrations of hydrofluoric acid and of zirconium varied.

Progress Report No. 11 presents more data in the area of Progress Report No. 8. Although data for all concentrations of zirconium for the complete temperature range are not available for every initial hydrofluoric acid concentration, sufficient information (Tables IC to VC of Progress Report No. 8 and Tables I to IV of Progress Report No. 11) is now available to set up a system of control based on density measurement. The possible precision of measurement is indicated by the fact that a change of 0.0001 density unit corresponds to a zirconium concentration change of 0.0008 molar unit.

II. Determination of the Relationship of Electrical Conductivity to Fluoride Concentration. Progress Report No. 9 describes the technique used in the electrical conductivity measurements and presents data for a group of zirconium fluoride solutions at 25°C.

Further work on these measurements was begun, but it was requested that this phase of the investigation be discontinued, partly because, as pointed out by the Idaho Falls group, the sufficiently rapid analytical methods for zirconium and fluoride available as a consequence of the work previously indicated minimized the need for the density and electrical conductivity measurements of zirconium fluoride - hydrofluoric acid solutions.

III. Determination of the Relationship of Specific Gravity to Stainless-Steel Concentration. Progress Reports Nos. 1 and 2 present specific-gravity and density measurements at four temperatures for a variety of solutions containing 347 stainless steel dissolved in sulfuric acid. For control purposes, the following linear equation can be used for determining the composition of solution derived from a given sulfuric acid solution.

$$D \text{ of Soln} = D \text{ of Acid} + K \text{ (Steel Concn)} ,$$

where "D of Soln" is the density of the solution at the temperature of measurement; "D of Acid" is the density at the same temperature of the original acid solution before any steel was dissolved in it; "K" is a constant characteristic of the original acid concentration, the temperature of measurement, and the nature of the steel; and "Steel Concn" is the concentration of dissolved steel in appropriate units.

The possible precision of measurement is determined by the fact that 0.0001 density unit corresponds to about 0.07 gram of dissolved steel per liter of sulfuric acid solution.

In this phase of the work, the general method and two specific cases, i.e., two samples of steel, have been investigated.

C. RESEARCH REPORTS ISSUED

The following research reports have been issued in the form of Progress Reports, on the subject matter indicated.

Progress Report	Date	Subject
No. 1	June, 1953	Densities of solutions of 347 stainless steel dissolved in sulfuric acid
No. 2	August, 1953	Densities of solutions of 347 stainless steel dissolved in sulfuric acid
No. 3	August, 1953	Densities of solutions of hydrofluoric acid
No. 4	September, 1953	Amperometric titration of zirconium
No. 5	September, 1953	Photometric determination of aluminum
No. 6	September, 1953	Indirect polarographic determination of fluoride
No. 7	September, 1953	Summary of analytical procedures for fluoride solution
No. 8	September, 1953	Densities of solutions of zirconium in hydrofluoric acid
No. 9	September, 1953	Conductometric data for solutions of zirconium in hydrofluoric acid

Progress Report	Date	Subject
No. 10	September, 1953	(Project 2121-2, on Kinetic Studies)
No. 11	February, 1954	Densities of solutions of zirconium in hydrofluoric acid
No. 12	February, 1954	Amperometric titration of sulfate
No. 13	February, 1954	Photometric determination of nitrate
No. 14	February, 1954	Possible interference in analytical procedures for fluoride solution
No. 15	February, 1954	Polarographic determination of chromium and iron
No. 16	February, 1954	Summary of analytical procedures for sulfuric acid - nitric acid solutions of 347 stainless steel