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SUBJECT: Spectrophotometric Studies of Solutions at Elevated Temperatures
and Pressures: Status and Program for FY-1961 and Part of FY-1962

TO: D. E. Ferguson and M. T. Kelley

FROM: R. E. Biggers and J. M. Chilton

ABSTRACT

The Oak Ridge National Laboratory has initiated under AEC Activity 5310 a program on the spectrophotometric study of aqueous solution chemistry whose goal is operation at temperatures up to at least 330°C and at pressures up to 200 atmospheres, and to near the critical point if this appears to be feasible. A spectrophotometer capable of operation under these extreme conditions is being designed and developed by an outside subcontractor. The instrument, after necessary development, may provide an in-line analytical system for fluid fuel reactors for high temperature-pressure processes, and will serve as an important tool for basic chemical research. This program will extend the fundamental high temperature spectrophotometric work now being pursued under AEC Activity 5330 to these applications.

Three phases of an experimental program to parallel and aid the subcontract development work, and which will lead to the eventual use of such equipment with nonstatic systems, has been previously described in more detail. The over-all aims of this program, and that part of it using a miniaturized loop system, are to determine the limitations of absorption spectroscopic methods of analysis of many kinds of light and heavy water solutions, of uranyl sulfate and other HRT type solutions, and to study the chemistry and kinetics of these systems at elevated temperatures. The problems and dynamics of carrying out spectrophotometric measurements on circulating liquid streams will also be investigated. In particular, the problems associated with gas equilibration and the separation of gas from the liquid phase prior to measurement, and the effect of and means for the removal of suspended solid particles will be studied. At the same time, it is desirable to further develop methods for resolving (with computer aid) the very complex spectra of such multi-component systems.

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ABSTRACT (Continued)

Negotiations have been completed between UCNC (ORNL) and the Applied Physics Corporation of Monrovia, California, for the subcontract work, which consists of the study, development, and detailed design of a complete spectrophotometric system to be used with highly alpha-active solutions at high temperatures and pressures. The subcontract has been in effect about 3.5 months and is proceeding smoothly and well on schedule. Approximately 85 engineering drawings have been prepared to date, and an approximate design has been arrived at for almost all of the entire complex system. A somewhat new type of cell has now been designed and the construction of a test cell is scheduled in the very near future. The optical design of the entire complex system is essentially complete. The cell system is unique in many ways, and has such design characteristics that we anticipate little or no trouble in reaching our goals of temperature and pressure.

The design of a complete miniaturized circulating loop system has now been completed by the design sections of the Chemical Technology and the Engineering and Mechanical Divisions. This miniature loop system is designed to be used in conjunction with a standard Cary Model 14PM Recording Spectrophotometer without any modification of the instrument. The upper limits of temperature and pressure are not expected at present to exceed 150°C and 8 atmospheres, with provision for using gas overpressures.

With static solutions in thermostated cells, spectral studies have been made on uranium, copper, and nickel sulfate, and perchlorate systems as a function of temperature and other solution variables up to 100°C, and at atmospheric pressure. As soon as the other equipment becomes operable, the operating conditions of the experimentation will be increased, with respect to temperature and pressure. The experimentation for uranium, plutonium, and some other systems has already been reported, in part.

A mathematical technique utilizing high-speed digital computation was developed to resolve the seriously overlapping spectral bands and fine structure. Spectra of uranyl perchlorate and uranyl sulfate have been completely resolved into the individual components. These techniques allow one to make a quantitative study of complex ion formation, etc., in solution as a function of temperature and other parameters. Intensive work, especially on the uranium spectra, shows that the least squares nonlinear, iterative, matrix programs that have been modified for this use are entirely adequate for the analysis of such spectral systems. It has been demonstrated that the computer programs can handle overlapping electronic and vibrational bands, and also electronic bands with vibrational fine structure. Correlation of these phenomena with complex ion formation, etc., is in progress.

At the present time an automatic digital data read-out system is being designed for the Cary Spectrophotometer and should be operating within six months. It will feature IBM card output with simultaneous wavelength and absorbency punched, in addition to other miscellaneous data. The circuitry will be constructed from ferrite magnetic core modules insofar as this is possible. Data can be obtained at wavelength intervals as close as 1 Å.

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A: Purpose and Goals

The purpose of this program is to develop techniques for studying the fundamental chemistry of aqueous solutions of uranium, other transuranium elements, some of the lanthanides and fission products, and other elements of interest at temperatures in excess of 100°C, and of various mixtures of these substances. A spectrophotometer capable of operating up to 330°C and at pressures up to at least 200 atmospheres with highly radioactive (alpha) solutions will be constructed and designed by the Applied Physics Corporation of Monrovia, California. It is hoped that the system will be operable up to near the critical point of light and heavy water systems. The application of this instrument to unique analytical problems connected with high temperature radioactive processes will be investigated. Studies will also be made of solubilities, reaction rates, and valence state distributions as a function of temperature and other conditions. Fundamental studies of the effects of solution variables and temperature on the parameters of the spectra will yield information concerning the role that complex ion formation, hydrolysis, temperature, etc., play in the chemistry of the systems. The spectrophotometer will serve both as an analytical and a fundamental research tool.

An ultimate goal of the program will be to study the application of such a suitably modified instrument to provide an in-line analytical system for high-temperature high-pressure fluid streams, and for chemical research studies of such systems. Utilization of the spectrophotometric technique at high temperatures and pressures will provide a means for determining not only equilibrium conditions but also the kinetics of the reactions in such systems without the complexities and the uncertainties introduced by utilizing withdrawal of a large number of samples. Many of the analytical values determined for the constituents of aqueous solutions at high-temperature are always questionable if the sample is reduced to room temperature before the determinations are made, since solubilities, valence states, adsorption, etc., of ions most often change with temperature. For the extension of this technique to fluid fuel streams of nuclear reactors or other intensely radioactive streams, a study and calculations have been made on the effect of Cerenkov radiation on spectrophotometric measurements.¹⁸ The results indicate that certain features, different from normal design, must be met before such a system could be operable.

Three phases of an experimental program to parallel and aid the subcontract development work and which will lead to the eventual use of such equipment with nonstatic systems has been described in more detail in a previous memo¹ and elsewhere.^{2,3} This program will extend and supplement the other fundamental and applied high temperature spectrophotometric work now being pursued at ORNL under AEC Activity 5330.

B: Program Budget

As of the present date, the following budget figures apply to this program; they are detailed and discussed elsewhere.²

Program and Budget Proposal for "Spectrophotometric Studies of Solutions at Elevated Temperatures and Pressures"

	<u>FY-1961</u>	<u>FY-1962</u>
Normal Program Cost	\$65,000	\$125,000
Unusual Costs		
a. Computer Analysis	15,000	20,000
b. Auxiliary Spectrophotometric Equipment	20,000	25,000
	<hr/>	<hr/>
Total	\$100,000	\$150,000
ORNL Man-years	2.0	3.0

Subcontract Costs: not completely included in the above budget figures.

Depending upon the rate of progress on various phases of the over-all program it will be necessary to increase the manpower on the program. Even at the present time the manpower is not sufficient to handle the various phases of the program nearly as well as would be desirable.

C: Subcontract Between ORNL and the Applied Physics Corporation

1. Review

In a previous memo¹ it was stated that if subcontract arrangements could be made on the proposed schedule the work on the high-temperature high-pressure spectrophotometer system would be started on March 1, 1959, and be installed by October 1, 1960. Unfortunately, the negotiations were delayed by many difficulties, predominantly of a legal nature, for about 13.5 months. Highlights of a part of these difficulties have been summarized.^{4,5}

As of March 14, 1960, negotiations were completed between UCNC (ORNL) and the Applied Physics Corporation of Monrovia, California. Their work consists of the study, development, and detailed design of a complete spectrophotometric system to be used for work with highly radioactive (alpha) solutions at high temperatures and pressures.

The system will conform to the detailed specifications⁶ drawn up by members of the staff at ORNL, and will employ all of the other results and progress made in this field at ORNL in recent years. The study, design, and development subcontract (UCNC Purchase Order 91X-44900C, March 14, 1960) is expected to not total more than \$51,513.00 (limit for fixed fee). After agreement is reached concerning a particular design and the complete drawings are finished, the system will be constructed by an outside subcontractor and then installed. The system will be based on the general characteristics and design features of the Cary Model 14PM Automatic Recording, Ultraviolet-Visible-Near Infrared Spectrophotometer, modified in such a manner that the entire system meets the specifications.⁶

2. Present Status

The subcontract has been in effect about 3.5 months and is proceeding well on or somewhat ahead of schedule, and more than 85 engineering blueprints for the system have been prepared to the present date. An approximate design has been arrived at for almost all of the entire complex system. The persons concerned have conceptual ideas regarding most of the more important aspects of the operation of the system. A somewhat new type of cell has now been designed and construction of a test cell is scheduled in the near future. The optical design is essentially complete. The cell system is unique in many respects and has such design characteristics that we anticipate little trouble in reaching our goals of temperature and pressure.

The final detailed design drawings should be finished by December 31, 1960. Construction should start early in 1961 and will require about 8 months, followed by an estimated two or three months of installation and testing. It is hoped that the system will be operating by November 1, 1961, and not later than early in 1962.

Among the most important parts of such a spectrophotometric system and the most difficult to design and construct are the optical windows for the cells. A thorough survey of the literature, and problems encountered in the design and use of windows for optical measurements at elevated temperatures and pressures, was recently made by the authors.⁹ The design and development work on this problem, in addition to that already done at ORNL, will be carried out by the Applied Physics Corporation in such a manner as is necessary to provide cell windows that will be safe and leak-proof at temperatures above 250°C. The immediate temperature goal is 330°C, but serviceability up to essentially the critical point (372°C) will also be studied.

Solutions of both radioactive and nonradioactive materials will be investigated at temperatures up to 330°C or higher, and under high pressure. This initial work will be predominantly of a fundamental nature but will be closely related to other programs at ORNL which deal with aqueous solutions at elevated temperatures. After the successful demonstration of the reliability and adequate characteristics of the high-temperature high-pressure system with cells operated in the static manner, means for operation in a loop system will be studied. It is expected that the results obtained with a simpler

loop described below, and operated at moderate pressure and at temperatures not higher than 150°C, will greatly simplify and facilitate the extension of the high-temperature high-pressure system to loop or flowing stream operation.

D: Spectrophotometric Studies with Circulating Loop Systems

The design of a complete miniaturized circulating loop system has been completed by the design sections of the Chemical Technology and the Engineering and Mechanical Divisions. Complete drawings are available.⁷ This miniature loop system is designed to be used in conjunction with a standard Cary Model 14PM Spectrophotometer without any modification of the instrument. The loop volume will be about 500 ml or less, with a variable circulation rate up to about 3 liters/min. A cell window design^{8a} adequate for the maximum temperature and pressure expected is used in this loop system. The upper limits of temperature and pressure are not expected, at present, to exceed 150°C and 8 atmospheres total pressure. The loop has many useful features and is designed with adequate provisions to handle added gas overpressures. It features a filtering system, design for gas bubble removal, a sample container system for contacting the loop liquid with corrosion specimens or particulate matter, and entry to the loop while operating.

The over-all aims of this program using the miniature loop are to determine the limitations of absorption spectroscopic methods of analysis of many different kinds of solutions, including uranyl sulfate and other HRT type solutions, especially at elevated temperatures. The problems and dynamics of carrying out spectrophotometric measurements on circulating liquid streams will be investigated. In particular, the problems associated with gas equilibration and the separation of gas from the liquid phase prior to measurement, and the effect and means of the removal of suspended solid particles will be carefully studied.

The general type of studies to be carried out with this system has been described.^{1,3} This system will enable some of the proposed design features of the special spectrophotometer to be evaluated before construction begins, and special features designed into the miniature loop system will allow one to determine the requirements and limitations of making spectral measurements on circulating streams. The fundamental chemistry of such systems as mentioned above will be studied with this technique and also with the aid of Raman spectral measurements. The construction of the miniature loop system is scheduled to start on September 8, 1960, and is planned to require about six weeks. The complete instrumentation for this miniature loop system is under development.

E: Present and Recent Work

1. Spectral Studies

With static solutions in thermostated glass cells, spectral studies have been made on uranium, copper, nickel sulfate, and perchlorate systems as a function of temperature and other solution variables. The experimentation for uranium, plutonium, and other systems has been reported¹⁰ in part, and more completely in the references listed therein.

The characteristics of the spectra of the actinides, lanthanides, and other transition group elements of interest are such that the treatment of spectral data from very complex multicomponent systems is quite practical. However, the solution of this problem is completely insurmountable without the use of high-speed digital computation, especially for seriously overlapping spectral bands, and various transitions that are observed. Studies of these problems have been undertaken to demonstrate the feasibility and practicability of extending such measurements to temperatures higher than 100°C. The most complicated item in this system is the uranyl spectrum. The serious overlapping of the uranium bands and the fine structure observed, coupled with the fact that the individual transitions react in different ways (e.g., changes in absorption peak frequencies, bandwidths, and peak intensities) to changes in temperature or solution parameters, complicate the spectra even further. A mathematical technique utilizing high-speed digital computation was developed to resolve the seriously overlapping spectral bands and fine structure. Spectra of uranyl perchlorate and uranyl sulfate have been completely resolved into the individual components. These techniques permit one to make a quantitative study of complex ion formation, etc., in solution as a function of temperature.

Intensive work, especially on the uranium spectra, show that the least squares, nonlinear, iterative matrix programs used are entirely adequate for the analysis of such systems. It has been demonstrated that the computer programs can handle overlapping electronic and vibrational bands, and also electronic bands with vibrational fine structure. Correlation of these phenomena with complex ion formation, etc., is in progress.^{10a} A detailed report on the use of high-speed computing for this purpose is being prepared.¹²

In connection with the present project, work is about to begin on a program of study on the polymerization and hydrolysis of plutonium in uranyl nitrate and nitric acid solutions at elevated temperatures. This planned work has recently been thoroughly reviewed and discussed from the point of view of health hazards, health physics procedures, personnel safety, and experimental procedures.¹¹ The present state of knowledge concerning the polymerization of plutonium was reviewed and a detailed suggested program

of study was discussed. Previous work, both at ORNL and elsewhere, and a detailed description of the facilities set up for the investigation and the mode of operation of all of the equipment was also discussed therein.

2. Mathematics and High-Speed Digital Computation

Earlier work¹⁰ has shown that it is possible to determine spectrophotometrically the concentrations (e.g., the valence states of plutonium, uranium, etc.) of numerous species, under definite solution conditions at a given temperature, by the use of suitable simultaneous equations, and standard computer codes for their solution. Detailed consideration of the over-all spectra of the actinides (including the various valence states), lanthanides, and some of the transition metals, and of the general sharpness of the absorption spectral bands, shows that the technique should be useful for large multicomponent systems. However, such techniques become very complicated when the solution conditions or temperature are varied, and especially if uranium is present. A technique has been found for resolving the overlapping spectral bands of such systems. A recent lecture¹⁷ at ORNL was concerned with a complete review and discussion of these problems.

An iterative, generalized, least-squares fitting matrix routine that has been written¹³ for the ORACLE computer (the high-speed, general-purpose digital computer at ORNL) for x-ray diffraction calculations has been modified for the purpose of resolving the complex spectra. A similar, though not as useful, program is available for the IBM-704.¹⁴ Three parameters suffice to define a given spectral band: the intensity parameter, the band-width parameter, and the frequency or position parameter (in millimicrons or cm^{-1}). When the data for the summed observed spectrum (absorbency vs frequency) together with estimates of the parameters that determine the spectral bands are supplied, the computer program can resolve the summed curve into its individual components on the basis that the individual spectral bands are all governed by the same general type of mathematical function, which is probably correct at least to a very good first approximation for very many cases.

Much study and literature review has been given to the most appropriate functions for representing the shapes of various single spectral bands and to what factors contribute to the broadening of the "line" into a band in the condensed systems that liquids represent. Suffice it to say here that a Gaussian type function has been found to be one of the best functions to use. Jorgensen¹⁵ has reached essentially the same conclusion. The Gaussian model does not give a perfect fit on the tails of the bands, and some of the factors that cause broadening of the spectral lines may be somewhat better described by a resonance-type function. Resolutions based on such resonance-type functions were carried out on the IBM-704, and these results show that although the fit on the tails of the spectral bands may be somewhat better than the Gaussian fit, the fit at the peak is much worse (too narrow) and that overall, the Gaussian model is by far the better model. Jorgensen¹⁵ has also concluded that resonance-type models are not applicable. A review of most all of the confusing literature on this subject has indicated that a more nearly theoretically correct model would probably be a

function combining a Gaussian (or probability) function with a small contribution from a resonance function.

At the present time there is, however, insufficient space in the fast memory of the ORACLE (2,048 words) or the available IBM-704 (8K, or 8,192 words) to set up the matrix program for a double function with the presently available generalized least-square matrix program. A fast memory of at least 15,000 words capacity would be required for such a program concerned with up to 12 to 13 peaks and 54 to 65 variable parameters. When the IBM-7090 (32K, or 32,768 word fast memory) is installed (late fall, 1960) we plan to investigate the use of other single and double functions to fit absorption band contours, and for the analysis of complex multicomponent systems. For a system containing 20-25 spectral bands a considerably larger fast memory than that of the IBM-704 is required. The IBM-7090 should be adequate. The present ORACLE program can analyze up to 21 peaks (3 parameters each), and the operator can also specify which parameters are to be varied (in any combination) up to 51 varied parameters.

Much use has also been made of the programs available for ORACLE regarding linear simultaneous equation problems, the Bairstow Iteration Polynomial Equation Solver, the Linear Regression and Correlation Code II, and many other varied programs. Other computer programs have been written¹⁶ which will take the final parameters calculated for the resolved bands of any spectral system and generate the data according to a given band model. The error at each point and its summation is also generated. This data can then be obtained in an output form, which when printed yields tabular data according to any format that is desired. Or, on the other hand, one can specify that the data are to be plotted on the ORACLE Curve Plotter. The x-axis may be plotted either as cm^{-1} , or wavelength, and the y-axis may be either absorbency or molar absorbency index. The axes are labeled accordingly and other information such as title, date, etc., put on the curve plotter scope. Either the resolved bands, the summed, calculated, and/or the observed spectrum or both may be plotted. The summed fitting error (+) can then be plotted on a second picture vs either cm^{-1} or wavelength.

Work is beginning on the conversion of practically all of the computer work from ORACLE to the IBM system so that work can proceed smoothly and rapidly when the IBM-7090 is installed within a few months. This is desirable in view of the forthcoming automatic digital data spectrophotometer output system that is discussed below. In addition, "Least Squares II" is to be rewritten for the IBM system, and the NLLS¹⁴ code (an IBM-704 program for fitting nonlinear curves by least squares) will probably be revised by its author for the IBM-7090 with the incorporation of a number of desired changes and additions. A code will also be written for the IBM-7090 for the Spectral Analysis of Multicomponent Systems using the least squares method in matrix form. This differs from the conventional linear simultaneous equation applications, particularly in the possibility for the inclusion of many more analytical wavelengths than components, with attendant increases in precision and accuracy.

3. Automatic, Digital, Data Output System for Cary Spectrophotometer

At the present time an automatic, digital, data read-out system is being designed and should be operating within six months. It will feature IBM punched card output with simultaneous wavelength and absorbency punched in pairs, in addition to other miscellaneous data. Data can be obtained at variable wavelength intervals as close as 1 Å. The spectra are obtained with a Cary Model 14PM Automatic Recording Ultraviolet-Visible-Near Infrared Spectrophotometer, and very ample instrumental resolution is available even for very fine structure of the lanthanide and actinide elements. At present, the spectra are recorded on a 30 Å/in. of chart basis (can be expanded) on a linear wavelength scale, and the data for the computer programs are obtained by hand therefrom at 10 Å intervals.

The output shafts for wavelength and absorbency (on a 20-in. folded scale), the digitizers, and the digitizer interrogation controls will be supplied and installed by the Applied Physics Corporation. However, a study is under way on a system that would eliminate the need for digitizers and permit the data to be dumped out directly in decimal form on cards via an IBM printing card punch. If the digitizer system is used, the data must be dumped out in binary form. The control system, intermediate memory storage, parameter system, etc., for a punched card output package system is being designed by the Computer Development and Engineering Group of the Instrumentation and Controls Division at ORNL. The circuitry is being constructed from ferrite magnetic core modules insofar as this is possible. If binary output is used, a nonprinting, binary, IBM card punch will be used for the data output; otherwise a printing decimal punch (Hollerith Code) will be used. It is thought that a packing density of 16 data point pairs per card is feasible for binary output, and about 7 data point pairs for decimal output. It appears that the unit should be capable of the output of approximately 350 points per minute.

An automatic digital output system is also planned for the high-temperature, high-pressure spectrophotometer under development by the Applied Physics Corporation. This elevated temperature spectrophotometer system will feature spectral data output in 3 forms simultaneously. They are: the spectrum on a strip chart, linear in wavelength; Log Extinction Coefficient (Absorptivity) chart record; and digital output of wavelength and absorbency data point pairs (along with other scalars and miscellaneous data as may be necessary) on IBM punched cards.

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