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GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF RESEARCH ADMINISTRATION

RESEARCH PROJECT INITIATION

Date: 15 March 1973

Project Title: "Improvement of Extraction - Photometric Techniques"

Project No: G-33-658

Principal Investigator Dr. H. A. Flaschka

Sponsor: National Science Foundation

Agreement Period: From March 1, 1973 Until August 31, 1974

Type Agreement: Grant No. GP-37476X

Amount: \$32,300 NSF Funds (G-33-658)
5,305 GIT Contribution (G-33-345)
\$37,605 Total

Reports Required: Interim Progress

Sponsor Contact Person (s):

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Assigned to: School of Chemistry

COPIES TO:

Principal Investigator

School Director

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Director, Research Administration

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Photographic Laboratory

Project File

Other _____

GEORGIA INSTITUTE OF TECHNOLOGY
Office of Contract Administration

SPONSORED PROJECT TERMINATION

No Action
OK
Page 2
Date: March 23, 1976

Project Title: Improvement of Extraction - Photometric Techniques

Project No: G-33-658

Project Director: Dr. H. A. Flaschka

Sponsor: National Science Foundation

Effective Termination Date: 3/31/76 (Grant Exp.)

Clearance of Accounting Charges: by 3/31/76

Grant/Contract Closeout Actions Remaining:

- ☐ Final Invoice and Closing Documents
- ☒ Final Fiscal Report
- ☐ Final Report of Inventions
- ☐ Govt. Property Inventory & Related Certificate
- ☐ Classified Material Certificate
- ☐ Other _____

Assigned to: Chemistry (School/Laboratory)

Copies to:

Project Director
Division Chief (EES)
School/Laboratory Director
Dean/Director-EES
Accounting Office
Procurement Office
Security Coordinator (OCA) ✓
Reports Coordinator (OCA)

Library, Technical Reports Section
Office of Computing Services
Director, Physical Plant
EES Information Office
Project File (OCA)
Project Code (GTRI)
Other _____

Interims Report No. 1

Re: NSF Grant: GP 37476X1

Principal Investigator: H. A. Flaschka

School of Chemistry, Georgia Institute of Technology
Atlanta, Ga. 30332

Date Due: March 1, 1974

Although the various areas of research under the Grant are closely inter-related to achieve the final goal "Improvement of Extraction-Photometric Techniques", they will be dealt with separately, because different workers are engaged in the details.

Solid and Homogeneous Extraction. Several more compounds have been investigated as extracting solvents but none of those showed any great advantage over compounds already in use.

Long-Path Photometry. Several determinations have been performed using the long-path photometer at hand to show versatility and limits of the machine and to possibly find points where further improvements could be made. Iron was determined on the 6-8 ppb level using Ferrozine as the reagent without enrichment. A 20-cm cell gave 0.039 absorbance reading for 10 ppb in the calibration. The low absorbance values can be used reliably because of the extreme stability and low noiselevel of the instrument. The instrument was also used for performing photometric titrations on the trace level. Among other successfully completed titrations it is worthwhile to mention 3 ml each of 10^{-7} F Cu(II) titrated with PAN, 10^{-7} F Ca titrated with EDTA in the presence of excess Murexide to create a selfindicating system and of 10^{-6} F Fe(II) with periodate stabilized permanganate. All titrations were performed with accuracies and precisions well comparable to those executed on much higher concentration levels.

Long-Path Cells. Several new ways of constructing longer cells of smaller diameter have been tested. Success has been met with and some of the ways have been described in a publication already submitted in reprint form to NSF. In connection with the modular monochromator a multiple reflection cell has been designed and built. The prototype is used to evaluate the various parameters influencing the effectivity of the cell and better models are in the state of designing. A laser was of great help to study the reflection paths because of its highly collimated beam.

LED's and Phototransistors.

As new types of LED's become commercially available they are tested for use as light source in photometry. Some of the results of these investigations have been published. Reprints have already been submitted to NSF.

Portable Instrument.

The Iron-Ferrozine reaction was made the basis of a field determination for Fe(II) in natural waters to be performed in situ. Employing a green LED as light source-monochromator portion and a phototransistor and a 15-cm small volume long-path cell it was possible to assemble the complete photometer including battery powerpack in a box with dimensions of 18 x 12 x 6 with a small microamperemeter on top of it included. Analytical performance of the instrument was excellent. Stability high, noiselevel low, calibration curve straight even with an electronic log converter incorporated, and practical handling very easy. The instrument is to be taken in actual field use by the Geology Department for limnological investigations.

Liquid Pressure Chromatography.

These portions of the project got started late because of the long delivery time for the instrument. Once set up the machine had to be broken in (as well as

the operators) and after various breakdowns and adjustments finally worked. Based on the results of initial trials additional components, column, detector etc., had to be purchased. Eventually the hoped for break-through came and separation of the PAN complexes of Cu, Co, and Ni was achieved. Although not yet satisfactory the indication is clear that the way is correct and doubts about the final practicality of the approach cannot longer exist.

Respectfully submitted,

H. Flaschka, Ph.D.
Regents' Professor of Chemistry

J. A. Bertrand, Director
School of Chemistry

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

CHEMISTRY

Improvements of Extraction-Photometric Techniques

Interims Report No. 2

RE: NSF GRANT GP 37476X1

Principle Investigator: H. A. Flaschka

School of Chemistry, Georgia Institute of
Technology, Atlanta, Ga. 30332

Date due: March 5, 1975

The attempts to achieve separation of various metal complexes of PAN (pyridyl-azo-naphthol) have not been satisfactory. In part because the liquid chromatograph resisted vehemently to get in working condition the easy way and later broke down several times and in part because the PAN system seems not to lend itself very well to the intended separations. We are in the process of switching to other organic chelating agents, like acetylacetone and dithiozone.

Long-path photometers have been very successfully applied to the photometric titrations of extremely small amounts of material. A paper on the subject has been accepted by Microchem. J. and is scheduled for publishing in the March 75 issue.

Applications to some special situations are under investigation and very promising results have been obtained in two cases, which at the present time are under closer study. Almost finished is the development of a method for the determination of chromium in blood serum, with only 0.5 ml serum being required. Adequate absorbance readings are obtained in a 20-cm cell. The method has found much interest at the Center for Disease Control. A manuscript draft will soon be initiated. The other study involves the following. Many reagents for photometric determinations exist that show satisfactory properties in all respects except a high absorptivity of the entity to be finally subjected to the photometric measurement. Here long-path photometry should be the remedy. As a test case the determination of manganese as the Mn(III) triethanolamine complex (green) is being studied and the situation is such that we have reached the limit due to losses of manganese by adsorption on

the glass walls. Smaller amounts of manganese can be determined with the new method than with the standard method involving oxidation to permanganate. And, very important for practical applications, chloride and most organic materials do not interfere. Publication state of this investigation should soon be reached.

Progress has also been made in the field of improvement of cell construction. The long fragile glass cells showed an annoyingly high rate of breakage. This situation is now fully remedied by encasing the cell, often together with light source and photodetector, into plastic, liquid polymer is poured on it and cured. Quite helpful as light sources for field use are Light Emitting Diodes (LED's). A paper has been published on this topic and reprints have already been submitted. A long-path field instrument has been developed that is presently being used by the Geology Department for routine determinations of iron in lake and stream waters. Great improvement in sensitivity is expected from the application of the recently developed phototransistors with one amplifier stage already on the same semiconductor chip.

Trace analysis is greatly plagued by the introduction of impurities during processing the samples either from reagents or environment or both. Simplification in the analytical method and reduction of steps in the procedure should be a remedy in such cases. A study was undertaken with fusion opening under heat lamps and sample dissolution by isothermal diffusion of hydrochloric or nitric acid under reduced pressure. A report on the successful conclusion of these investigations has been accepted by Z. Anal. Chem. and is in press.

Respectfully submitted

H. Flaschka, Ph.D.
Regents' Professor - Chemistry

A. Bertrand, Ph.D.
Chairman, School of Chemistry

1-32-658

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

CHEMISTRY

Final Technical Report

NSF Grant MPS72-05105

March 20, 1976

Principal Investigator, H. A. Flaschka

Respectfully submitted,

H. A. Flaschka, Ph.D.
Principal Investigator

The interim report mentioned the difficulties experienced when setting up the liquid chromatograph. Finally the instrument was ready and separations of metals were attempted. According to the proposal very unselective reagents were employed such as PAN, PAR and dithizone. Great efforts and many man hours were expended but the results were extremely meager. Even the complexes of metals of differing valencies like e. g. iron(III) and copper(II) could not be made to function as expected. It seems that the best way to achieve the set goal would be to effect the separation of the metals in the absence of the colorimetric agent (e.g. on an ion exchange column) and only after separation to add the reagent for making detection more sensitive. Unfortunately, this requires expansion for the instrument to at least another pumping device and column. Some preliminary trials were performed on borrowed equipment and showed the possibility to be workable. However, the original simplicity of the approach would be lost and this loss seemed not to be outweighed by whatever was gained. Thus the project was temporarily dropped and will be taken on again in the future by another group of students.

To apply a long-path cell in the detector of a liquid chromatograph, however, showed very promising results and has great possibilities for practical application. The data will be part of the Ph.D. thesis by M. Coulter and a publication should soon be written. Reprints will be submitted when available.

As was pointed out in the proposal the combination of solid-state devices with long-path microcells should offer great advantages for building simple and rugged but still sensitive instruments, especially valuable in field use. One of such instruments was designed and constructed with the special dedication to the determination of iron in waters. The description of the apparatus and the performance tests and

and their results will be subject of a paper in preparation and constitute also a part of Coulter's thesis. The instrument was used by the Geology Department of Georgia Tech during environmental field studies and exceeded the already high expectations set on it. The LED employed for the iron determination emits light that should also be suitable for determining phosphorous; after a readily effected exchange of LEDs manganese could be determined. These further investigations into the instrument will be conducted by special project students in the coming Spring Quarter. While this is already past the termination date of the grant the studies as well as several others mentioned below are still considered as part of the grant work, and will be reported later on in form of reprints of the respective publications.

The use of long-path microcells in photometric titrations was investigated, especially with the intent to find out how low in amounts and concentrations one could go. The results are reported as part of the Ph.D. thesis of D. Paschal and are the topic of a publication of which the reprints have already been submitted.

The basic idea of employing solid-state devices in photometry and some of the very simple circuits involved have already been dealt with in the first publication on the subject. Reprints have been submitted. During further studies, especially with devices made commercially available afterwards, it became clear that in order to derive the full benefit from the devices it would be necessary to study some of their properties more closely. It must be realized that LEDs are designed and rated for their original purpose, namely, as indicators for various instruments, especially calculators. The ratings are, therefore, given with regards to

parameters important for such application and where appropriate in photoptic units that relate to the sensitivity of the human eye. Therefore, studies of parameters important for application in photometry and transformation of rating data from photoptic to physical units are necessary in order to obtain the basis for appropriate evaluation. For gathering the relevant data, circuits were developed that permitted testing of LED and photodetectors, especially of the photodiode and phototransistor types. The evaluations led to improved utilization and allowed design of optimal circuits for power supply, adjustments, amplifications and regulation. A manuscript describing results and circuits is in its final state and should soon be submitted for publication. Recently new photoptic devices have become available. With those and the electronic and mechanical parts accumulated from the grant funds the investigations will continue beyond the termination data and reprints of papers submitted. These investigations have been and will be greatly aided by the advice in electronic matters from Mr. G. O'Brien.

When driving the concept of long-path microcells to the limit difficulties arise in several respects. Most of those are related to the fact that the diameter of the cell bore becomes increasingly smaller, and the cells longer and longer. Cell breakage increases and alignment due to bending causes trouble. These two problems found a surprisingly simple solution due to a fine idea by Coulter, namely, to cast the cell into a plastic block. This also eliminates easily the following problem. When the cell bore gets smaller the space between the side opening (where the filling arm connects to the cell bore) and the cell window is difficult to fill and empty and thus becomes a dead volume of significance. With the casting technique it is possible to attach ducts to the cell end

and affix windows with gaskets and held by screws, and thus eliminate the dead volume. It also becomes simple to attach LED and detector without glue but rather in a way that makes changes quite easy. When the cell bore becomes smaller, then less light can enter from the luminous area of the LED and only a fraction of the sensitive area of the detector is illuminated. Several possibilities exist to overcome the difficulties, e.g. application of fiber optics or spacing the detector from the cell. It was, however, decided to increase the out-put of the LED. This cannot be accomplished simply by increasing its power current, because then danger of damage becomes imminent. But even when damage is avoided the energy conversion is impaired. The way out is to pulse the LED. Then for a short period high current can be applied giving a higher light out-put and in the dark period cooling takes place. Of course, under these conditions the detector must be phase sensitive and receive only during the light pulse period. This approach has an added benefit; with pulsed light, meticulous exclusion of ambient light is no longer necessary, and working in the open is possible, a feature quite welcome especially in field work.

The longer the cell and the smaller the bore, the greater the mismatch between volume of the liquid in the cell and the area of cell walls in contact with the liquid. Thus losses due to adsorption on the glass become a point of significance. The situation is under investigation by Mrs. S. Slaton as part of her M.S. thesis. The system under study is the triethanolamine complex of manganese. In addition to the adsorption study, the system is of great practical analytical importance. With a long-path cell manganese can be determined at levels employed commonly with the permanagante photometry method, but with the distinctive advantage of no interference by chloride and no heating required.

The study is almost finished and a publication will soon be written.

During the investigations dealing with trace analysis it was realized that many samples required opening and that thereby danger of contamination exists. It was, therefore, deemed appropriate to investigate the possibilities to reduce the problem. Isothermal dissolution of fusion cakes or even certain sample materials, and heat lamp fusion were found to be some of the remedies. These studies were part of the Ph.D. thesis of G. L. Myers and have already been published. The reprints have been submitted several months ago.

One further possibility to drive determination of traces to even lower levels is application of amplification. This was demonstrated on the determination of chromium in blood serum. The standard photometric method involving the dichromate diphenylcarbazide complex and requiring 5-10 ml sample was scaled down to a microdetermination with a long-path cell consuming only 0.2 ml sample which, when processed to a final volume of 2 milliliters, yields a comfortable absorbance reading of about 0.03 in a 20-cm cell for a normal serum with 25 ng Cr/ml. The molar absorptivity of the dichromate-diphenylcarbazide complex is 31,000 l/mole-cm which value is about the same as that of the quinone diimine of o-tolidine (30,200) which can be obtained by oxidation of o-tolidine by dichromate. Strictly stoichiometric oxidation is achieved with the manganese(III) pyrophosphate as a mediator as reported by Berak and Barka (Anal. Lett., 6, 585 (1973)). At first glance with the absorptivity values nearly equal there seems to be no advantage in switching from diphenyl carbazide to o-tolidine. However, one must consider the "apparent absorptivity", that is, the absorptivity per mole chromium. This for the diphenylcarbazide is then only $31,000/2 = 15,500$ because of 2 Cr per $\text{Cr}_2\text{O}_7^{2-}$,

while that with the o-tolidine becomes $30,200 \times 1.5 = 45,300$ since one dichromate oxidizes three o-tolidines thus producing 1.5 diimines per chromium. Under the improved conditions it is now possible to shorten the path-length or further reduce the sample volume or operate with higher absorbance values. During the o-tolidine study it was found that vanadium reacts in a similar way and an expansion of the approach to this metal is planned. The chromium determination is the main part of the Ph.D. thesis of S. Yarbro which is just going to press. Publications are in the working stage and reprints will be sent when available.