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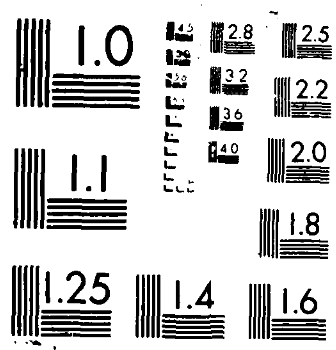
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DEVELOPMENT AND EVALUATION OF INSTRUMENTATION AND METHODS FOR MULTI-ELEMENT ANALYSIS

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Technical reports submitted to ONR during contract term:

Technical Report #	Title
1	A Selective Spectral-Line Modulation Technique for High Sensitivity Continuum Source Atomic Absorption Spectrometry
2	Automatic Background-Correcting Spectrometer
3	Saturation of Energy Levels in Analytical Atomic Fluorescence Spectrometry - I. Theory
4	Spectral and Noise Characteristics of a 300-W Eimac Arc Lamp
5	A Modified Microwave-Induced Plasma (MIP) Discharge Chamber Exhibiting High Stability and Immunity from Sample Solvent Extinguishment
6	Physical Characterization of a New Atom Cell for Atomic Spectrometry: The Helium-Oxygen-Acetylene Flame
7	Report on Combined Meeting of the XX Colloquium Spectroscopicum Internationale and 7th International Conference on Atomic Spectroscopy
8	Simplified Apparatus for Routine Selective Spectral-Line Modulation Atomic Absorption Spectrometry
9	Enhancement of Pneumatic Nebulization Efficiency Through Application of an Electric Field
10	A New, Accurate Method for the Measurement of Rise Velocities in Laminar Flames
11	Atomic Emission Spectrometry of Trace Metals Using a New Kind of Microwave-Induced Helium Plasma at Atmospheric Pressure
12	Biennial Review on Flame Emission, Atomic Absorption, and Atomic Fluorescence Spectrometry for *Analytical Chemistry*
13	Development and Characterization of a Miniature Inductively Coupled Plasma Source for Atomic Emission Spectrometry
14	Investigation into the Operating Characteristics of a Microarc Atmospheric-Pressure Glow Discharge
15	Microwave-Supported Discharges

16 Theoretical Study of the Spatial Distribution of Atoms Surrounding an Individual Solute Particle Vaporizing in an Analytical Flame

17 Measurement and Comparison of Relative Free-Atom Fractions in the Helium-Oxygen-Acetylene Flames

18 Comparison of Atomic Fluorescence Power Efficiencies for the Helium-Oxygen-Acetylene and Air-Acetylene Flames

19 Wide-Bandwidth Analog Correlator and Its Application to Mode-Locked Laser Measurements

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22 Characteristics of the Background Emission Spectrums from a Miniature ICP

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24 An Accurate Model for Sample Droplet Acceleration in Analytical Flames

25 Correction of Quenching Errors in Analytical Fluorimetry Through Use of Time Resolution

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27 Reduction of Spectral Interferences in Flame Emission Spectrometry by Selective Spectral-Line Modulation

28 Development and Characterization of a 9-mm Inductively Coupled Argon Plasma (ICP) Source for Atomic Emission Spectrometry

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32 A Novel Device for the Accurate Dispensing of Small Volumes of Liquid Samples

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49 Approaching the Limit in Atomic Spectrochemical Analysis

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60	Mini, Micro, and High-Efficiency Torches
61	A Detailed Consideration of Resonance Radiation Trapping in the Argon Inductively Coupled Plasma
62	A New Method for Obtaining Individual Component Spectra from Those of Complex Mixtures
63	Vaporization in the Absence of Ionization of Alkali Chloride Particles in a Laminar Air-Acetylene Flame
64	Development of a Microwave Induced Nitrogen Discharge at Atmospheric Pressure (MINDAP)
65	Analytical Characteristics of the Microwave Induced Nitrogen Discharge at Atmospheric Pressure (MINDAP)
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102	A Novel Light-Scattering Technique to Study Gas-Flow Dynamics in an ICP Torch

103 Determination of Subnanosecond Fluorescence Lifetimes with a UHF Television Tuner and a CW or Mode-Locked Laser

104 An Improved Uniform Size Droplet Generator

105 A New Technique for the Elimination of Fluorescence Interference in Raman Spectroscopy

106 Temporally and Spatially Resolved Studies in an Amplitude Modulated ICP

107 Taming the Surfatron

108 Analytical Characteristics of a New, Versatile Inductively Coupled Plasma-Mass Spectrometer

109 Morphological Investigation of Solute Particles Trapped from an Air-Acetylene Flame

110 The Use of Sample Modulation to Simplify the Experimental Arrangement of Selective Line Modulation in Atomic Emission Spectrometry

111 A Detailed Study of Noise Sources in Selective Line Modulation Atomic Spectrometry

112 A Modulated Sample-Introduction System for ICP-Atomic Emission Spectrometry

List of Publications Emanating from Contract

1. "Automatic Background-Correcting Spectrometer", Anal. Chem. 48, 2030-3 (1976) (with R. J. Sydor and J. R. Sinnamon).

2. "A Selective Spectral-Line Modulation Technique for High Sensitivity Continuum-Source Atomic Absorption Spectrometry", Anal. Chem. 49, 98-105 (1977) (with R. L. Cochran).

3. "Influence of Droplet Desolvation, Particle Vaporization and Atomic Diffusion on the Distribution of Atoms in Analytical Flames and Plasmas", Bulletin of the Technical University, Prague, Czechoslovakia, 113-23 (1977) (with C. B. Boss).

4. "Physical Characterization of the Helium-Oxygen-Acetylene Flame as an Atom Cell for Atomic Spectrometry", Anal. Chem. 49, 2013-8 (1977) (with K. A. Saturday).

5. "Spectral and Noise Characteristics of a 300-W Eimac Arc Lamp", Anal. Chem. 49, 2040-3 (1977) (with R. N. Cochran).

6. "Saturation of Energy Levels in Analytical Atomic Fluorescence Spectrometry--I. Theory", Spectrochim. Acta 33B,79-99 (1978) (with D. R. Olivares).

7. "Determination of Trace Metals by Microwave Plasma Spectrometry with an Atmospheric Pressure Helium Discharge", Anal. Chem. 50, 1257-60 (1978) (with A. T. Zander).

8. "A New, Accurate Method for the Measurement of Rise Velocities in Laminar Flames", Appl. Spectrosc. 32, 377-80 (1978) (with C. B. Boss).

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12. "Theoretical Study of the Spatial Distribution of Atoms Surrounding an Individual Solute Particle Vaporizing in an Analytical Flame", Anal. Chem. 51, 895-901 (1979) (with C. B. Boss).

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16. "Characteristics of the Background Emission Spectrum from a Miniature ICP", Anal. Chim. Acta 123, 319-24 (1981) (with R. N. Savage).

17. "Experimental Studies on Spatial Distributions of Atoms Surrounding an Individual Solute Particle Vaporizing in an Analytical Flame", Anal. Chem. 51, 1897-1905 (1979) (with C. B. Boss).

18. "Comparison of Atomic Fluorescence Power Efficiencies for the Helium-Oxygen-Acetylene and Air-Acetylene Flames", Anal. Chim. Acta 164, 51-66 (1984) (with K. A. Saturday and A. Yuen).

19. "Measurement and Comparison of Relative Free-Atom Fractions in the Helium-Oxygen-Acetylene Flame and Air-Acetylene Flames", Anal. Chem. 52, 786-92 (1980) (with K. A. Saturday).

20. "An Accurate Model for Sample Droplet Acceleration in an Air-Acetylene Flame", Anal. Chim. Acta 118, 293-9 (1980) (with R. E. Russo).

21. "Correction of Quenching Errors in Analytical Fluorimetry Through Use of Time Resolution", Anal. Chim. Acta 123, 255-61 (1981) (with G. R. Haugen).

22. "Reduction of Spectral Interferences in Flame Emission Spectrometry by Selective Spectral-Line Modulation", Anal. Chim. Acta 121, 165-74 (1980) (with S. W. Downey and J. G. Shabushnig).

23. "Effects of Gas Composition and Flame Sheathing on the Spatial Velocity Profiles of Laminar Analytical Acetylene Flames", Spectrochim. Acta 36B, 231-41 (1981) (with R. E. Russo).

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26. "Microwave-Supported Discharges", Appl. Spectrosc. 35, 357-71 (1981) (invited review paper with A. T. Zander).

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29. "Correlation Methods in the Chemistry Laboratory", American Laboratory 13, (3) 76-83 (1981) (with G. Horlick).

30. "Correlation-Based Approaches to Time-Resolved Fluorimetry", Anal. Chem. 53, 755-66A (1981) (with G. R. Haugen).

31. "Saturation of Energy Levels in Analytical Atomic Fluorescence Spectrometry--II. Experimental", Spectrochim. Acta 36B, 1059-79 (1981) (with Dorys Rojas de Olivares).

32. "Simple and Inexpensive Design for an Isolated Droplet Generator Useful in Studies of Atomization in Flames", Appl. Spectrosc. 35, 531-6 (1981) (with R. E. Russo and R. Withnell).

33. "Stochastic Photolysis: A New Method for Measuring Rates of Photosensitive Reactions", Appl. Spectrosc. 36, 203-9 (1982) (with G. R. Haugen, L. L. Steinmetz, and R. E. Russo).

34. "A New Instrument for Time-Resolved Reduction of Scattered Radiation in Fluorescence Measurements", Anal. Chim. Acta 134, 13-9 (1982) (with R. E. Russo).

35. "On the Significance of Radiation Trapping in the Inductively Coupled Plasma", Spectrochim. Acta 37B, 191-7 (1982) (with M. W. Blades).

36. "Determination of Atomic and Molecular Excited-State Lifetimes Using an Opto-Electronic Cross-Correlation Method", Appl. Spectrosc. 36, 92-9 (1982) (with R. E. Russo).

37. "Advances in Sample Introduction for Elemental Analysis", Industrial Chemical News 3, (1) 1 (1982).

38. "A New, Directly Computer-Controlled pH Stat", Anal. Chim. Acta 141, 173-86 (1982) (with R. E. Lemke).

39. "Microdroplet Sample Application in Electrothermal Atomization for Atomic Absorption Spectrometry", Anal. Chim. Acta 148, 181-92 (1983) (with J. G. Shabushnig).

40. "Reduction of Spectral Interferences in Inductively Coupled Plasma-Atomic Emission Spectrometry by Selective Spectral-Line Modulation", Anal. Chim. Acta 141, 193-205 (1982) (with S. W. Downey).

41. "Approaching the Limit in Atomic Spectrochemical Analysis", J. Chem. Educ. 50, 900-9 (1982).

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49. "Sample Introduction into the ICP by a Radio-Frequency Arc", Anal. Chem. 55, 1414-17 (1983) (with P. B. Farnsworth).

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54. "Mini, Micro, and High-Efficiency Torches for the ICP -- Toys or Tools?", Spectrochim. Acta 38B, 1465-1481 (1983).

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76. "Optical Imaging Spectrometers", Anal. Chem. 57, 2049-2055 (1985) (with J. W. Olesik).

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83. "Novel Techniques for the Determination of Fluorescence Lifetimes", Anal. Instrum. 14, 483-502 (1985) (with D. A. Wilson, and G. H. Vickers).

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85. "Time-Resolved Fluorescence With an Optical-Fiber Probe", Anal. Chim. Acta 192, 145-153 (1987) (with G. H. Vickers and R. M. Miller).

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87. "Electron Temperatures and Electron Number Densities Measured by Thomson Scattering in the Inductively Coupled Plasma", Anal. Chem. 58, 207-210 (1986) (with M. Huang and K. A. Marshall).

88. "A Fiber-Optic Absorption Cell for Remote Determination of Copper in Industrial Electroplating Baths", Anal. Chim. Acta 177, 121-128 (1985) (with J. Freeman, A. Childers, and A. Steele).

89. "A Modulated Sample Introduction System for Atomic Emission Spectrometry", Appl. Spectrosc. 40, 357-363 (1986) (with A. Steele).

90. "Twenty-five Years of Analytical Atomic Spectrometry", Anal. Chim. Acta 180, 69-98 (1986) (with S. Greenfield, N. Omenetto, A. Scheeline, and W. Slavin)

91. "A Steady-State Approach to Evaluation of Proposed Excitation Mechanisms in the Analytical ICP", Spectrochim. Acta, 41B, 683-697 (1986) (with G. D. Rayson)

92. "Use of Time-Resolution to Eliminate Bilirubin Interference in the Determination of Fluorescein", Anal. Chem. 58, 1225-1227 (1986) (with F. V. Bright and G. H. Vickers)

93. "A Computerized Tool for Studying Two-Dimensional Images of Spectroscopic Sources", Computer Enhanced Spectrosc. 3, 91-94 (1986) (with B. R. Hites, J. W. Olesik, and A. F. Parisi)

94. "A Novel Light-Scattering Technique to Study Gas-Flow Dynamics in an ICP Torch", Appl. Spectrosc. 40, 680-683 (1986) (with A. G. Childers)

95. "Determination of Subnanosecond Fluorescence Lifetimes with a UHF Television Tuner and a CW or Mode-Locked Laser", Appl. Spectrosc. 40, 683-687 (1986) (with F. V. Bright and D. A. Wilson)

96. "An Improved Uniform Size Droplet Generator", Appl. Spectrosc. 40, 688-691 (1986) (with A. G. Childers)

97. "Temporally and Spatially Resolved Studies in an Amplitude Modulated Inductively Coupled Plasma", Spectrochim. Acta 42B, 361-376 (1987) (with A. F. Parisi, G. D. Rayson, and J. W. Olesik).

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100. "Analytical Characteristics of an Inductively Coupled Plasma-Mass Spectrometer", Spectrochim. Acta 42B, 29-38 (1987) (with D. A. Wilson, G. H. Vickers, and A. T. Zander).

101. "Morphological Investigation of Solute Particles Trapped from an Air-Acetylene Flame", Appl. Spectrosc. 40, 939-944 (1986) (with A. G. Childers).

102. "The Use of Sample Modulation to Simplify the Experimental Arrangement of Selective Line Modulation in Atomic Emission Spectrometry", Appl Spectrosc. 40, 1110-1117 (1986) (with A. W. Steele).

103. "A Detailed Study of Noise Sources in Selective Line Modulation Atomic Spectrometry", Appl. Spectrosc. 40, 1117-1126 (1986) (with A. W. Steele).

104. "A Modulated Sample-Introduction System for ICP-Atomic Emission Spectrometry", Appl. Spectrosc. 40, 1127-1131 (1986) (with A. W. Steele).

105. "Torches for Inductively Coupled Plasmas" in Inductively Coupled Plasma Emission Spectrometry--Part 1: Methodology, Instrumentation and Performance, P.W.J.M. Boumans, ed., Wiley, 1987, 258-295 (with P.W.J.M. Boumans).

List of all people paid from contract N00014-76-C-0838 during contract period .

Bartelt, Joan
Blades, Michael
Bright, Frank
Carr, Jeffrey
Deutsch, Robert
Doherty, Michael
Downey, Stephen
Farnsworth, Paul
Freeman, James
Galante, Leonard
Hieftje, Gary
Hites, Bonnie
Lemke, Ralph
Lodder, Robert
Merrill, Dawn
Mitchell, Joel
Monnig, Curtis
Pak, Yongnam
Ramsey, J. Michael
Rezaaiyaan, Ruhangiz
Saturday, Kathy
Savage, Richard
Selby, Mark
Shabushnig, John
Steele, Andrew
Swarthout, Mary
Vickers, George
Weiss, Aaron
Wilson, Daniel
Wyatt, Wayde
Yuen, Anna
Zander, Andrew

This constitutes the final report of work accomplished under ONR contract N00014-76-C-0838. Over the ten-year period during which this contract was in force, a great deal was accomplished. As revealed earlier in this document, 112 technical reports were prepared, out of which has stemmed already 104 publications in refereed journals. Additional publications are still appearing and will be forwarded as they are received.

In addition, a substantial number of research personnel have been supported under this contract. A total of 9 Master's theses resulted from these studies, as did 14 Ph.D. theses. Also, 5 post-doctoral associates were funded, as were a number of part-time, clerical, and technical staff members.

Because of the wide range of activities that were pursued, it is difficult to summarize them here in a brief way. Instead, this report will concentrate on several highlights of the studies that have been completed to date. Importantly, a portion of this work is being continued under a new ONR contract, N00014-86-K-0366. In the following narrative, the papers cited are those listed elsewhere in this report under "List of Publications Emanating from Contract".

The principal focus of work pursued under the ONR contract just ending is to develop and characterize new methods for multielement analysis. Three such methods were originally emphasized and included the development of low-flow, high-efficiency torches for use in inductively coupled plasma (ICP) spectrometry, the exploration of novel microwave-induced plasmas (MIP) for elemental analysis, and the exploration of a new technique for the spectral selection of atomic or ionic emission lines, termed selective spectral line modulation (SLM).

Our studies to develop high-efficiency torches for ICP use have been highly successful and have resulted in systems that are now widely used in commercial instruments. This work has been reviewed in a journal (54) and a book chapter (105).

Our work with high-efficiency torches began with the development of miniaturized systems (10, 14-16, 24). In those studies, we progressed from a "standard" 18-mm torch, to 13-mm systems, and finally to a 9-mm device. By careful design, we were able to reduce thereby the gas-flow and power requirements for sustaining a usable plasma, and without loss of operating performance.

Later, we turned to a careful optimization of torch dimensions (…) and showed that it was possible to achieve the same kinds of reduction in operating power and gas flows but with a standard-size (18-mm) torch. This approach has the advantage of permitting the new high-efficiency torch to be employed with older ICP instruments. Performance of this kind of system was later evaluated (62, 73) and its application to miniaturized torches examined (75). It was found that there is little additional advantage to miniaturizing a fully optimized torch. Such optimized torches are now available commercially and at least two vendors of ICP instruments offer reduced-size torches patterned after our design.

Our studies into microwave-induced plasmas began with atmospheric pressure systems in helium (7) that have strong advantages over alternative argon-supported discharges or those that operate at reduced pressure. The characteristics of microwave plasmas were also reviewed (26). Because the key to successful operation of an MIP was found to be the delivery of a pre-vaporized form of the sample material, we turned our attention in part to the development and exploration of alternative sample-introduction techniques. The "microarc" system (11, 46) served nicely and was evaluated further (see below). Because of the high excitation energy available in the helium MIP, we found that it was useful not only for the excitation of metal atoms but also nonmetallic species (66-68). A more recent design (98), supported by a surface wave structure termed a "surfatron" offers even greater capability than our earlier MIP, supported by a resonant cavity device. We continue the exploration of this novel system under the new ONR contract.

In the course of our MIP explorations, we pursued the use of nitrogen as an inexpensive and conveniently available support gas. The resulting device, which we termed the "microwave-induced nitrogen discharge at atmospheric pressure" (MINDAP) (57-60) offers a number of attractive alternatives over the atmospheric pressure helium system. In particular, the MINDAP is a thermally hotter source, so that it can accept sample aerosols directly, without the need for pre-vaporization. In addition, the MINDAP produces a tail flame, much like the ICP. As a consequence, emission from it can be viewed in a side-on fashion rather than end-on, and background radiation from the plasma is minimized. In more recent investigations, we have found that the MINDAP is suitable also for use as an ionization source with mass spectrometry.

Our studies into the use of selective spectral line modulation (SLM) began with applying the technique to atomic absorption spectrometry (2) and to the selection of an appropriate light source to be used with the method (5). Later, we turned to the application of the method to atomic-emission spectrometry (22, 40, 103) and to improving the instrumentation used with the technique (102). An even more recent development, supported under the current ONR contract, makes SLM an extremely attractive alternative for eliminating spectral interferences such as those which frequently occur in ICP emission work.

Because of the importance of sample introduction to both ICP and MIP studies, and to the potential application of modulated sample introduction to the SLM procedure, we occupied a portion of our time pursuing novel sample introduction approaches. Early studies involved the enhancement of pneumatic nebulization efficiency by application of an electric field (9) and by using the microarc (11) described above. In addition, we constructed several microsampling devices (28, 32, [illegible]) and showed how sample could be introduced into spectroscopic sources in the form of uniform, discrete droplets that are less than one nanoliter in volume. A number of these studies have been reviewed ([illegible]). We learned later that samples could be introduced directly into an ICP by extracting a portion of the plasma energy and drawing it to a grounded sample (49). Recent investigations have shown that this "RF arc" technique is highly attractive for solid, conducting samples. Another potentially attractive approach to sample introduction involves the jet-impact nebulizer (52), which functions by directing a sample solution onto a solid surface. The kinetic energy of the jet is thereby converted into internal energy within the jet, so it is disrupted into a fine aerosol.

Lastly, we examined modulated sample-introduction systems for use with emission spectroscopic sources like the ICP (89, 104). Such systems served to modulate a sample and its signal but not a potentially interfering background level. As a consequence, the signal attributable to the sample can be extracted with the use of simple, frequency-selective amplifiers. Such systems are useful also in implementing the SIM approach (102).

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