Development and Evaluation of Instrumentation and Methods for Multi-Element Analysis

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

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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


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
Rezaaalyaan, 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 (SIM).

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 reductions 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 (48), 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 ORNL contract.

In the course of our MIP explorations, we pursued the use of nitrogen as an inexpensive and conveniently available support gas. Its 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 systems. 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 (7) and to the selection of an appropriate light source to be used with the method (17). Later, we turned to the application of the method to atomic-emission spectrometry (18, 40, 103) and to improving the instrumentation used with the technique (104). An even more recent development, supported under the current ORNL 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 microwave cells described above. In addition, we constructed several microsampling devices (28, 47, 40) and showed how sample could be introduced into spectrometric systems in the form of uniform, discrete droplets that are 1-2 microns in volume. A number of these studies have been described (40). We learned later that samples could be introduced directly into an ICP, extracting a portion of the plasma energy and directing 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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