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MASTER

TITLE STUDIES OF AN INDUCTIVELY COUPLED PLASMA WITH A FOURIER-TRANSFORM SPECTROMETER

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Studies of an Inductively Coupled Plasma with a Fourier-Transform Spectrometer

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Abstract

The inductively coupled plasma (ICP) excitation source for analytical atomic spectroscopy has been studied with the one-meter Fourier-transform spectrometer (FTS) located at Kitt Peak National Observatory, Tucson, Arizona. The high resolution of this spectrometer combined with the comprehensive wavelength coverage of the Fourier transform technique, allows the use of the spectra for elucidation of spectraphysical properties such as excitation temperatures and line widths. From these studies, the analytical applicability of the ICP-FTS combination is evaluated for atomic spectrochemical measurements in the visible and ultraviolet.

Introduction

Sensitive, efficient, and reliable multielement analysis is a goal of the modern analytical laboratory. Desirable characteristics such as high temperature, inert chemical atmosphere, and long term stability have made the inductively coupled plasma[1-4] the contemporary method of choice for multielement analysis by atomic spectroscopy. The ICP excitation source is an electrodeless argon plasma operated at atmospheric pressure and sustained by inductive coupling to a radiofrequency electromagnetic field. The standard frequency of operation is 27.12 MHz, and the standard power output is 1-3 kWatts.

Sample solution is introduced into the plasma in the form of a fine aerosol which is swept up through the central channel of the plasma by argon carrier gas flow. During a 2-3 millisecond residence time, the sample aerosol is desolvated, vaporized, atomized and ionized. The resulting free atoms and ions are electronically excited and emit characteristic radiation, allowing both qualitative and quantitative analysis. Two distinctive zones of the plasma are useful for analytical purposes: the initial radiation zone (IRZ) low in the plasma is a region of lower temperature where atomic emission is intense, and the normal analytical zone (NAZ) higher in the plasma is a region of higher temperature where ionic emission is observed and the best sensitivity is attained for most elements.

For analytical applications, an ICP source is usually interfaced to a wavelength dispersive (grating) spectrometer: either a scanning monochromator or a direct-reading polychromator. The scanning system offers flexibility in wavelength selection, but requires longer analysis time and more sample consumption. Direct-reading polychromators offer advantages of speed and true simultaneity, but wavelength selection has been predetermined and is difficult to change. An ideal spectrometer for the ICP would combine the characteristics of comprehensive simultaneous wavelength coverage, accurate wavelength and intensity determination, large linear dynamic range, good signal-to-noise ratio, fast analysis time, and high resolution.

Non-dispersive multiplex techniques such as Fourier transform spectrometry have proven to be valuable tools for spectral investigations in the infrared. Although the "multiplex" or Fellgets advantage is only realized in the infrared where detectors are detector-noise limited, other advantages of multiplex techniques can be realized in the visible and ultraviolet regions of interest to analytical atomic spectroscopy. Optical and mechanical technology for interferometers in the visible and ultraviolet is new and more demanding than for the infrared. However it is accessible, and the one-meter FTS at Kitt Peak[5] is capable of high resolution operation down to 250nm.

The purpose of this study was to explore the potentials and problems of the ICP-FTS combination for basic spectraphysical studies of the ICP source and to assess the analytical applicability of the instrumental merger. Important preliminary work in this field has been conducted by Horlick, Yuen, and Hall[6,7].

Experimental

The Kitt Peak Fourier transform spectrometer is based on a folded Michelson interferometer design with a total optical path difference of one meter. "Cats eye" retroreflectors are used to reduce errors arising from tilt or wobble in the mirror system. The internal path is housed in a vacuum chamber. The instrument is capable of operating in the range 250nm to 16.5μm with wavenumber accuracy on the order of 10^{-3} cm^{-1} and resolution capability on the order of 10^5. In this study, an ultrasil fused silica beamsplitter with aluminum coating and blue-enhanced diode detectors were used, except in the near infrared for which indium antimonide photodetectors were used.

A Plasma Therm model 2500 ICP unit was transported from Los Alamos to Kitt Peak where it was secured in front of the 10mm spectrometer aperture on a heavy-duty tripod which allowed up-down movement of the torch box and consequently of the plasma image on the spectrometer aperture. An optical magnification factor of 5.3 allowed very precise selection of small volumes of the plasma for spectral observation. The ICP was operated at conditions intended to simulate normal analytical operation. Spectra were observed in six vertical zones from 2-25mm above the induction coils of the ICP torch (Figure 1). Spectra of an iron solution (480-550nm) recorded in each of the six zones were used to determine an excitation temperature profile of the plasma. Spectra of a multielement solution of 22 common analyte elements (290nm-1.7μm) recorded at varying concentrations in the IRZ (6mm above the induction coils) and in the NAZ (16mm above the induction coils) were used in the analytical studies.

Temperature Determinations

Knowledge of the temperature of an excitation source in analytical spectroscopy is important for understanding desolvation, dissociation, atomization, ionization, and excitation processes occurring in the source. The powerful information gathering ability of an FTS makes it quite suitable to such basic spectraphysical studies. Spectroscopic excitation temperatures can be derived by the "slope method" by measuring the relative intensities of several transitions of the same element and constructing "Boltzmann plots" of $\ln (I\lambda^3/gf)$ versus upper energy level (Figure 2). The temperature is then derived from the slope $(-1/kT)$ of the resulting line. Iron was used as the thermometric species, and over 80 atomic iron transitions were identified in the spectra recorded in the six vertical zones of the plasma. The slope method relies on the use of oscillator strengths or gf values for the observed transitions. These values are available from several reference sources in the literature, but inconsistencies as great as an order of magnitude exist for the gf value of the same transition cited in different references. The gf values from four sources were used in this study,[8-11] and temperatures were calculated using each of these four references for each of the six plasma zones. Results are summarized in Table I. The gf values from reference (8) are known to be in error, but have been frequently used in the past; therefore they are included here for comparison, but have been eliminated from the calculation of average temperatures given in the last column. It can be noted that the calculated temperature for any given zone is critically dependent on the choice of gf values, which can produce variations greater than 10% of the average value. Nonetheless, the qualitative picture is consistent and represents an important contribution to the fundamental understanding of the ICP. Although a large number of previous studies of temperatures in the ICP have been published, it is only recently that a comprehensive spatial picture of the plasma has begun to emerge.[12,13]. In this study, excitation temperature was observed to be moderate (c. 5500K) low in the plasma, to increase to a maximum value (c. 7400K) in the NAZ at 10-1[illegible]mm above the induction coils, and to decrease again at higher vertical positions, dropping rapidly in value (c. 4200K) in the tail plume region.

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Spectral Line Widths

The measurement of spectral line widths in an excitation source is useful for the understanding of excitation mechanisms in the source and for the determination of spectral interferences in analytical work. Because of the high resolution required to make these measurements, very few studies of this subject have been previously reported for the ICP.[14-16] However, the high resolving power of the Kitt Peak FTS allowed the determination of line widths for 300 spectral lines of the 22 elements in the multielement solution studies, for 500 lines of iron, and for many lines of argon.

In the wavelength region 300-600nm, the widths of atomic and ionic lines were typically in the range .003-.006nm. Iron spectra recorded in the six plasma zones allowed a profiling of changes in line widths with vertical position in the plasma. Overall variations were slight, but line width maxima occurred in the zones between 5-12mm above the induction coils. For the near infrared region beyond 1μm, the observed line widths in the normal analytical zone were on the order of .02nm.

Temperatures calculated on the assumption of Doppler-limited line broadening were higher than the excitation temperatures derived from the slope method and were quite variable, indicating the existence of other line broadening mechanisms in the source. However, more detailed analysis of the line shapes is required for elucidation of this subject.

Analytical Applications

The analytical applicability of the ICP-FTS combination was investigated and assessed. Three hundred prominent lines of 22 elements and five hundred lines of iron in the wavelength range 290-600nm were identified. Line widths and relative intensities were determined for these lines. Linearity of the analytical working curves was verified for the concentration range 1-100 μg/ml investigated here. Detection limits in the ng/ml range were derived for 32 analytical lines in this spectral region.

Because of the multiplex nature of Fourier transform spectrometry (all the signal reaches the detector all the time), random noise in the source is evenly distributed throughout the baseline of the entire spectrum. That is, noise at all wavelengths in the spectrum is essentially constant, and the noise level at any given wavelength is dependent on the total concentration of all components in the sample. Detection limits in Fourier transform spectrometry therefore are dependent on i) total sample composition and ii) the relative intensity of the line selected for analysis, and can be defined as that concentration of analyte which corresponds to a signal on the standards working curve equal to twice the standard deviation (noise) of the baseline near the analytical wavelength in the sample spectrum (Figures 3,4).

The most significant advantage of the ICP-FTS combination is the comprehensive wavelength coverage (similar to that obtained with photographic plates) combined with extreme accuracy of wavelength and intensity determinations and large dynamic range. Thus, all the emission lines in the spectral region of interest are recorded, and the analyst can assess the spectral interferences and select the wavelengths to be used for quantitative determinations based on the information in the actual sample spectrum.

ICP Emission in the Near Infrared

Knowledge of ICP emission characteristics was extended into the near infrared to 1.7μm. The spectrum of the multielement solution in the normal analytical zone of the plasma was recorded, and prominent lines of the 22 elements and argon were identified with line widths and relative intensities. Although this region is rich in atomic argon transitions, several lines of oxygen, nitrogen, and alkali and alkaline earth elements which may be analytically useful were also identified.

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Conclusions

The ICP-FTS instrumental merger has been investigated for spectraphysical and analytical applications in the ultraviolet, visible, and near infrared. Advantages of the combined system include (i) a powerful information gathering tool for analytical and basic research studies (ii) comprehensive and simultaneous wavelength coverage allowing the selection of analytical lines based on information in the spectrum (iii) variable resolution (iv) accurate wavelength and intensity determinations (v) high optical throughput (vi) large linear dynamic range (vii) computer compatability of the digitized interferogram. Possible disadvantages include (i) the requirement of a stable light source, (ii) precise optical and mechanical requirements for visible and ultraviolet applications, (iii) distribution of noise in baseline can degrade detection limits in some cases (iv) requirement of a mathematically complex transform of the interferogram to a useful spectrum.

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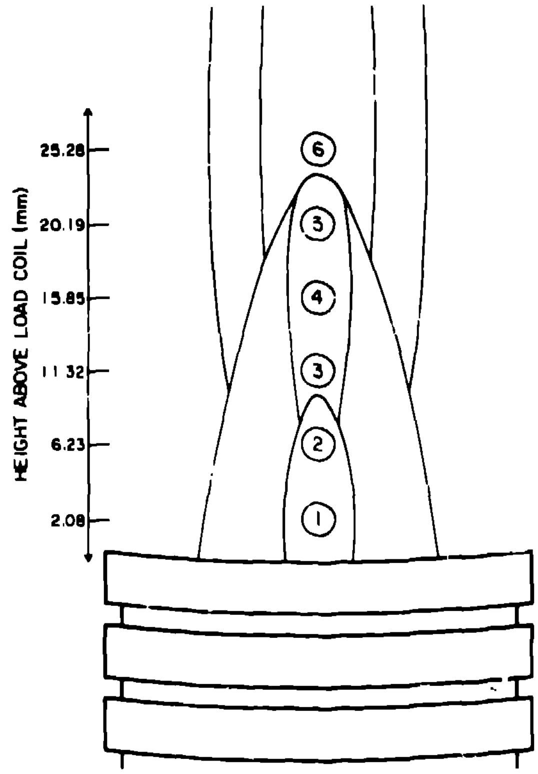

Figure 1. ICP zones for temperature profile.

EXCITATION TEMPERATURE

	gf(8)	gf(9)	gf(10)	gf(11)	AV TEMP (9), (10), (11)
ZONE 6	3629	4490	4083	4158	4237
ZONE 5	4788	6794	5636	5075	5702
ZONE 4	5134	7049	6134	5084	6087
ZONE 3	5404	7548	6298	8356	7401
ZONE 2	4214	6828	5587	6012	6077
ZONE 1	4678	6700	5519	5043	5571

Table 1. Iron Excitation Temperature Profile in the ICP, Using Four Different Reference Sets of gf Values for Each of the Six Vertical Zones

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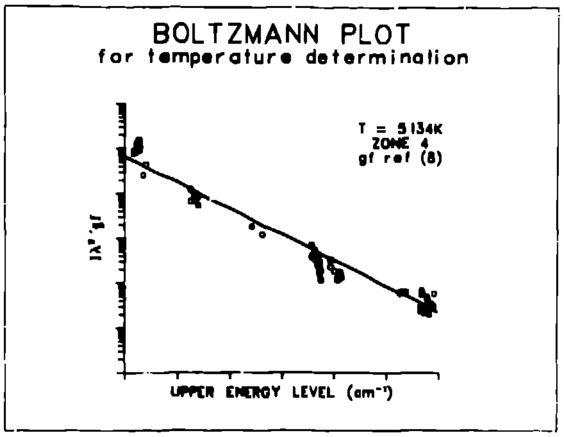

Figure 2. Boltzmann plot for temperature determination. Slope equals (-1/kT).

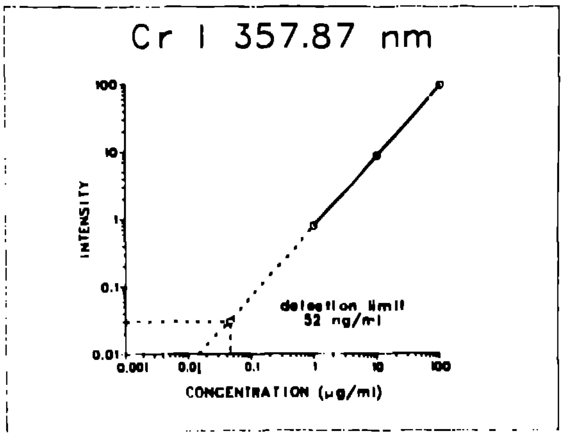

Figure 3. Analytical working curve for Cr 357.87 nm line. Extrapolation of standards curve for derivation of detection limit.

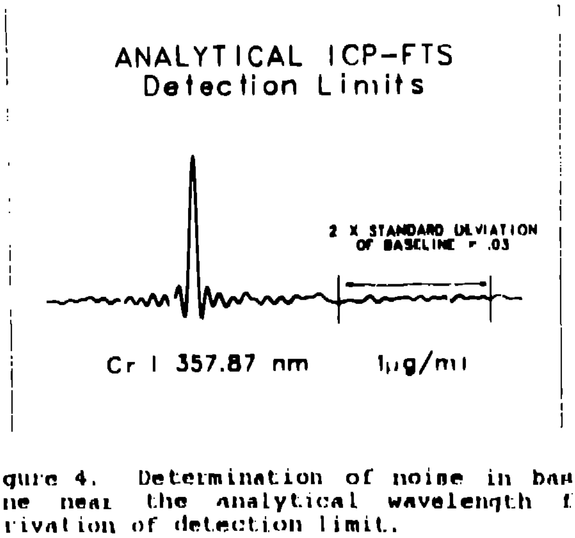

Figure 4. Determination of noise in baseline near the analytical wavelength for derivation of detection limit.