

# A continuous sampling air-ICP for metals emission monitoring

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## ABSTRACT

An air-inductively coupled plasma (air-ICP) system has been developed for continuous sampling and monitoring of metals as a continuous emission monitor (CEM). The plasma is contained in a metal enclosure to allow reduced-pressure operation. The enclosure and plasma are operated at a pressure slightly less than atmospheric using a Roots blower, so that sample gas is continuously drawn into the plasma. A Teflon sampling chamber, equipped with a sampling pump, is connected to the stack that is to be monitored to isokinetically sample gas from the exhaust line and introduce the sample into the air-ICP. Optical emission from metals in the sampled gas stream is detected and monitored using an acousto-optic tunable filter (AOTF) – echelle spectrometer system. A description of the continuous sampling air-ICP system is given, along with some preliminary laboratory data for continuous monitoring of metals.

Keywords: Continuous emission monitor, air plasma, ICP-AES, AOTF, echelle spectrometer

## 1. Introduction

The application of various plasma and electrical discharge sources for monitoring the elemental composition of aerosols, vapors, and airborne contaminants has a long history.<sup>1</sup> The energy available in a plasma source such as an inductively coupled plasma (ICP) is sufficient to vaporize and atomize all but the largest airborne particles and to excite these atoms to optically bright atomic and ionic states. The resulting optical emission is sufficiently intense and characteristic to identify and quantify all but a handful of the elements at trace levels.<sup>2,3</sup> The ICP is a uniquely useful source for these types of measurements due to its extremely high temperature, simplified operation at atmospheric and near atmospheric pressures, and relative insensitivity to changes in the sample matrix.

There are, however, a number of obstacles to the implementation of ICP – atomic emission spectroscopy (ICP-AES) for field applications, such as stack-gas monitoring and air monitoring. First, the standard laboratory-based ICP operates using argon for the plasma discharge gas as well as the gas carrying vapors, aerosols, or particles to the plasma. The use of argon necessitates a continuous supply of argon from cylinders or a dewar, either of which limit the mobility and untended operation of an ICP. Additionally, the argon ICP is somewhat sensitive to the addition of air, especially moist air, as the carrier gas for the sample material. One way to overcome these difficulties is to use air from a compressor as the plasma gas in the ICP. An air-ICP requires a larger power supply and an air compressor for operation, but requires only a small amount of argon when the plasma is ignited, requires no additional gas cylinders for continuous operation, and is easily operated with air or nitrogen as the sample or carrier gas. These characteristics make air-ICP-AES an excellent source for air and stack-gas monitoring.<sup>4-6</sup> The details of operation of the air-ICP have been described elsewhere.<sup>4,6</sup> Previous work using the air-ICP as a source for emissions monitoring has utilized an atmospheric-pressure plasma. Samples from the stack gas or air are drawn to fill a sampling loop, and valves are then switched and compressed air is used to force the sampled gases from the loop into the plasma. In this way, gas can be drawn isokinetically from a stack at high flow rates and injected at the lower flow rates needed for operation of the ICP.<sup>7,8</sup> This method has some problems including a duty cycle that limits the exposure times for the optical measurement to a few seconds, additional lost time during equilibration of the plasma, and the potential for drop out of particles at the slower velocity used for sample injection. For these reasons, we have developed a system that uses continuous sampling into a reduced-pressure ICP. Other work has used reduced-pressure plasmas to draw the sample gas directly into the plasma with no injection loop.<sup>9</sup> That system used a non-standard ICP torch, with the sample gas providing the entire plasma gas flow. This arrangement suffers from a number of limitations associated with self-absorption of the analyte emission lines at the cold boundaries of the plasma. This is the reason that standard analytical ICP torches have three concentric gas channels, with the analyte confined in the center of the plasma. Our work uses a standard three-channel ICP torch. For our reduced-pressure air-ICP system, gas is sampled isokinetically into an intermediate chamber. Gas from the intermediate chamber is isokinetically sampled again and is drawn into the plasma by the reduced pressure in the plasma

chamber. This system allows for continuous sample introduction with no dead time for loading a sample loop and waiting for the plasma to equilibrate to the sample during an injection cycle. This paper discusses the design and operation of this continuous sampling air-ICP system.

Another obstacle to the use of plasma and discharge sources for elemental analyses in field applications is the need for a high-resolution spectrometer that is also portable. A high-resolution spectrometer is required for three reasons. First, the gas streams that need to be monitored consist of relatively complex mixtures of elements with complex spectral interferences. For example, the presence of even moderate levels of iron in a sample stream will lead to such a large number and density of spectral lines that the sensitivity to minor components may be limited by spectral interferences without a spectrometer having high resolution. Second, the generation of a plasma in an air sample stream leads to the excitation of complex molecular spectra as well as atomic spectra. These dense molecular spectra will also limit the sensitivity of plasma emission techniques unless a high-resolution spectrometer is employed. Finally, the most sensitive or useful spectral lines of the materials that need to be detected or monitored may be so close to each other that a high-resolution system is required to monitor these materials at reasonable sensitivities and with confidence of unique identification. For example, two common heavy metals that are of environmental concern are Cd and As. These two elements have strong emission lines at 228.802 and 228.812 nm, respectively. With a separation of only 0.010-nm between peaks, these lines are only useful if they can be resolved. Also, for monitoring radionuclides, it is important to be able to resolve the emission features from different isotopes in order to measure not just concentration, but also the radioactivity, of a sample stream. For example, the activity of a sample containing U may be determined by resolving the naturally-occurring U-235 and U-238 isotopes, with emission features at 424.412 and 424.437, respectively.

Spectrometers with sufficient resolution to perform these tasks exist; however, they are large, heavy, expensive, delicate, and relatively slow for multielement monitoring. None of these characteristics make them suitable for field monitoring applications. These systems are large because, in order to obtain high resolution with a low-order grating, a long pathlength is required, typically 1- to 1.5-m. They are heavy because such a long spectrometer requires excellent mechanical stability in order to image a 10- to 20-cm slit over such a long distance without instability caused by vibration. This stability is achieved through sturdy mechanical frames and bulk (several hundred pounds). They are expensive because of the size of the components, including large high-quality optics. They are delicate because of the need for mechanical stability over such a long pathlength. Finally, they are relatively slow because the grating must be angle-tuned in order to detect spectral lines more than a few nm apart, even with an array detector such as a CCD. In previous work<sup>10</sup> we described a new high-resolution spectrometer that is small, light (46 lbs.), relatively inexpensive, and robust (with no moving parts), that can rapidly switch wavelengths across its spectral range. The spectrometer consists of an acousto-optic tunable filter (AOTF), an echelle grating spectrometer, and a CCD array detector. We are currently adapting this spectrometer for use as a simultaneous instrument rather than the rapid-sequential instrument described previously. This is being accomplished using an AOTF that selects three wavelengths simultaneously, by applying a multi-frequency RF drive signal to the device. Preliminary data for the multi-frequency AOTF – echelle spectrometer is presented.

## 2. Experimental

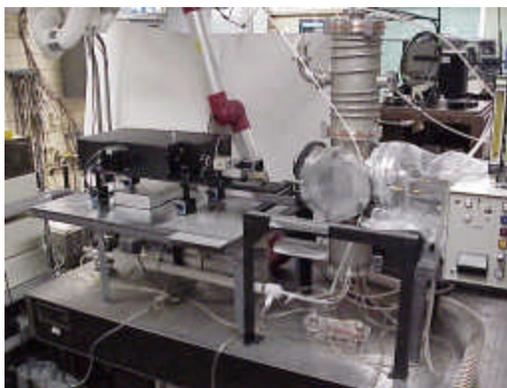


Figure 1. Photograph of the continuous sampling air-ICP system, including the ICP metal enclosure, part of the ICP automatching network (on the right side), the AOTF-echelle spectrometer (mounted on the angle-iron stand, on the left side), and the Teflon sampling chamber (below the stand, shown without the heat-tracing and insulation described in the text).

A photograph of the continuous sampling air-ICP system is shown in Figure 1. The system consists of an air-ICP that is operated at reduced pressure inside a 6"-diameter metal enclosure, a Teflon sampling chamber, and an AOTF-echelle spectrometer system that is used to detect ICP optical emission signals resulting from metals introduced into the plasma. The Roots blower, sampling pump, and ICP generator that are required for operation of the system are not shown in the photograph.

## 2.1. Enclosed ICP System

A schematic diagram of the enclosed ICP system and a photograph of the ICP torch, showing the connections to the automatching network (AMN) of the ICP generator system, are shown in Figure 2(a) and (b).

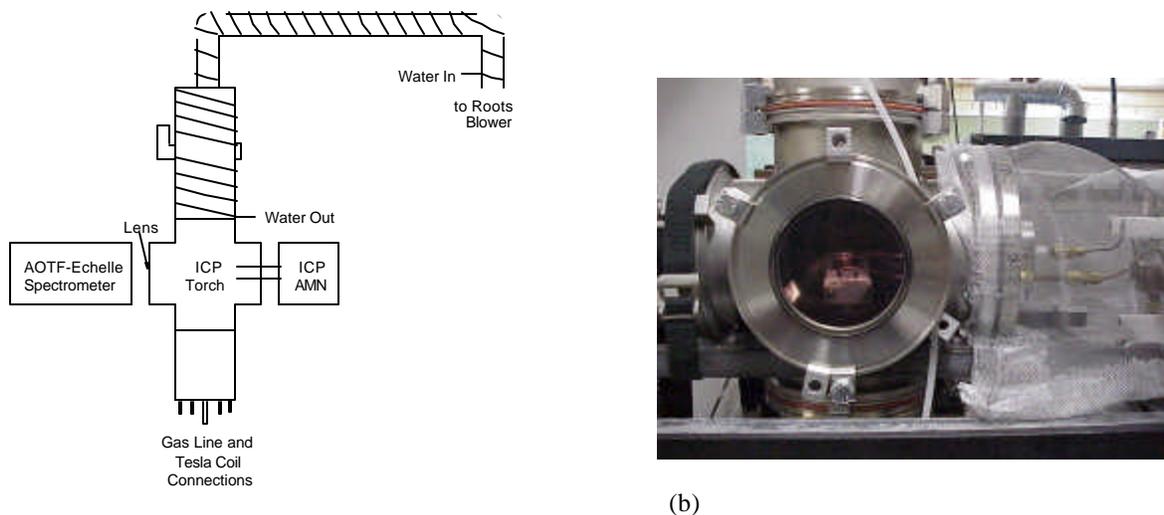


Figure 2. (a) Schematic diagram of the enclosed ICP system and (b) photograph of the ICP torch inside the 6"-diameter metal enclosure, showing the RF connections to the automatching network (AMN) of the ICP generator system.

The metal enclosure that is currently being used for the continuous sampling air-ICP system was originally developed for continuous monitoring of alkali metals in coal and biomass combustion and in gasification process lines, by flame emission spectroscopy. The system has been modified for ICP operation by making provisions for mounting the ICP torch inside the 6"-diameter stainless steel 6-way cross and providing the required ICP gas line, Tesla coil, and AMN connections. The metal enclosure is comprised of standard 6"-diameter (ISO 160) stainless steel vacuum components (Huntington Labs and MDC Vacuum Products Corporation). The bottom flange of the enclosure has gas-line connections for the ICP torch plasma and auxiliary gas supplies and for the ICP axial channel (sample) gas, which is connected to the Teflon sampling chamber. A connection point for the Tesla coil discharge required to ignite the ICP is included on the bottom flange of the enclosure. An additional gas-line connection on the bottom flange is provided for the introduction of supplemental air (60-80 liters per minute, lpm), which provides some cooling of the metal enclosure during operation of the 3-kW air plasma. The supplemental air passes through a glass sparging tube (Thomas Scientific) inside the metal enclosure to disperse the air throughout the bottom of the enclosure. Above the ICP torch, 1/4"-diameter stainless steel tubing is welded onto the 6"-diameter metal enclosure, for water-cooling of the upper portion of the enclosure. At the top of the enclosure, 1.5"-diameter stainless steel tubing (also water-cooled) is connected. The Roots blower (assembled by Grubb Equipment Corporation, St. Paul, MN) is connected to this 1.5"-diameter tubing to operate the enclosure at reduced pressure, 0 to -5 psig, in order to draw sample continuously into the plasma, from the sampling chamber, through the axial channel of the ICP torch.

The AMN of the ICP generator system is connected to the load coil of the ICP torch by copper tubing that passes through a 6"-diameter (ISO 160) bolt flange, on the right side of the 6-way cross, as shown in Figure 2(b). (The AMN is cut-off on the right side of the photograph.) The high-voltage RF electrode is a length of 1/4"-diameter copper tubing that passes through the center of a 1/4"-diameter Teflon Swagelok bulkhead union feed-through that is mounted in the center of a Delrin flange (identical to an MDC ISO 63 stainless steel clamp flange), on the right side of the 6-way cross. The Teflon and Delrin isolate the RF voltage from the grounded stainless steel flange, thereby preventing arcing from occurring at the point where

the RF electrode passes through the flange. The ground electrode is a length of 1/4" copper tubing that passes directly through the stainless steel flange. Swagelok reducing unions are used to connect the two electrodes to 1/8"-diameter copper tubing, for connection to the AMN and to the ICP load coil, which is a 3-turn coil. The load coil and connecting copper tubing are cooled by water flowing through the tubing, as is typical for ICP systems. With the current arrangement, no RF arcing has occurred at the interface between the AMN and the metal enclosure. Initially, a commercial ceramic RF feed-through was used. However, this feed-through failed due to arcing within the connector or to mechanical failure (breakage) of the ceramic, and was replaced with the current arrangement. As shown in Figure 2(b), grounded steel mesh, bolted to the chamber and AMN, is used to shield the operator from high RF fields and prevent incidental contact with high voltage components.

## 2.2. Teflon Sampling Chamber

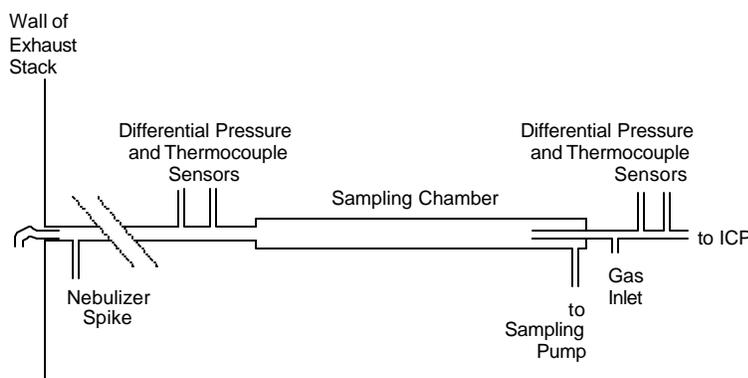


Figure 3. Schematic diagram of the Teflon sampling chamber, with connection to an exhaust stack.

The sampling arrangement for the air-ICP system consists of a dual-stage sampling technique. A diagram of the system is shown in Figure 3. A glass-lined sampling probe is connected to the stack to extract a gas stream from the stack. A port consisting of a Teflon tee is provided so that metal aerosols generated using a pneumatic or ultrasonic nebulizer can be introduced into the sample gas stream, in order to perform on-line calibration of the air-ICP system. The gas flows through a Teflon tube to the inlet of the sampling chamber. There are two ports (Teflon tees) that are provided for connecting a differential pressure transducer and a thermocouple, so that the gas flow rate and temperature at the inlet to the sampling chamber can be monitored. The outlet end of the chamber consists of a Teflon sampling tube and an exhaust line. There are two ports that are provided for connecting a second set of differential pressure and thermocouple sensors, so that the gas flow rate and temperature at the outlet of the sampling chamber (the inlet to the axial channel of the ICP torch) can be monitored. An additional port is provided as a gas inlet for argon that is used only during start-up of the plasma.

A high-volume primary sample is drawn isokinetically from a process pipe using a standard commercial EPA isokinetic glass-lined probe that has an integral heater (Apex Instruments). The nozzle on the probe is a standard source-sampling nozzle with a 1/2"-inner diameter; the glass liner of the nozzle has a 5/8"-outer diameter. The outlet of the glass liner connects through an adapter to a 1/2" Teflon Swagelok tee. The side port of this tee is used for injection of calibration aerosol into the sample stream (nebulizer spike in Figure 3). The in-line port of this tee is connected to a commercial heat-traced Teflon line (Technical Heaters) that is 1/2"-outer diameter and 12' in length (not shown in Figure 3). The outlet of the heat-traced line is connected to a Teflon differential pressure flow cell. The flow element consists of a 1/4"-inner diameter tube that is 2" long. A Teflon-coated thermocouple (Omega Engineering) is inserted into the inlet of the flow cell to monitor the gas stream's temperature. The differential pressure is monitored using a differential pressure transducer (Valdine, model P55D), which has a maximum range of 3.5" of water. The outlet of the primary flow cell is connected to the inlet of the sampling chamber, which is a Teflon tube that is 1"-inner diameter and 24" in length. A lubricated vane pump (Gast Manufacturing, model 0523-V4-G180DX) draws the sample through the chamber in a laminar-flow arrangement, with over 95% of the sample being removed through an exit port and exhaust line at the end of the chamber.

A secondary sample is drawn isokinetically from the gas flowing through the sampling chamber using a 1/4"-outer diameter Teflon sampling tube that is inserted approximately 4" into the end of the chamber. The tube currently used has a 0.170"-inner diameter, with a 30° taper at the sampling end. This tube can easily be exchanged for a tube with a different inner diameter to accommodate different sample velocities in the exhaust stack and still allow appropriate sample flow into

the ICP torch. The secondary sample outlet is connected to a 1/4" Teflon Swagelok tee. The in-line port of this tee is followed by another Teflon differential pressure flow cell, to monitor the sample flow rate into the reduced-pressure air-ICP. The flow element in this cell consists of a 0.094"-inner diameter Teflon tube that is 1.25" long. A second Teflon-coated thermocouple is inserted into the inlet of this flow cell. The differential pressure is monitored using an oil-filled manometer (Dwyer Instrument, model 101) that has a maximum range of 0.5" of water. The primary flow cell, Teflon sampling chamber, and secondary flow cell are heat-traced using electrical heat tape and insulation wrap. The sample flow from the outlet of the secondary flow cell passes through the bottom of the reduced-pressure chamber (metal enclosure) and into the axial channel of the ICP torch. The pressure in the chamber is reduced slightly below atmospheric pressure, to draw an appropriate sample flow, approximately 1 lpm, into the axial channel of the torch. The chamber is evacuated using a Roots-type pump (Roots Division, Dresser Industries, universal RAI model 22) that has a 1 horsepower variable speed motor.

### 2.3. AOTF-Echelle Spectrometer

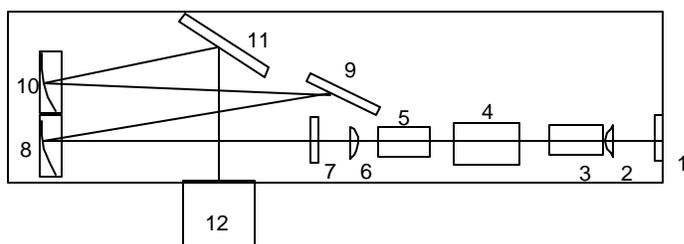


Figure 4. Schematic diagram of the AOTF-echelle spectrometer. The numbered components in the schematic are (1) input aperture, (2) collimating lens, (3) polarizer, (4) AOTF, (5) polarizer, (6) imaging lens, (7) slit, (8) collimating mirror, (9) echelle grating, (10) focusing mirror, (11) flat folding mirror, and (12) detector.

An acousto-optic tunable filter (AOTF) – echelle spectrometer system is used to detect optical emission signals from metals introduced into the air-ICP. A 2"-diameter, 3" focal-length fused silica lens, mounted in the flange on the 6-way cross between the air-ICP and the AOTF-echelle spectrometer, forms a 1:1 image of the plasma at the input aperture of the spectrometer. A description of the design and capabilities of the AOTF-echelle spectrometer, including the resolution of the spectrometer and ICP-AES limits of detection for metals introduced into argon and air plasmas has been published.<sup>10</sup> The quartz AOTF (that is placed between two crossed polarizers) acts as an order-sorting pre-filter for the echelle spectrometer. An RF frequency applied to the AOTF selects a narrow band, less than 1-nm bandwidth, of optical emission from the ICP. This light is introduced into the echelle spectrometer. The bandpass of the AOTF is smaller than the width of one order of the echelle grating, so no cross-dispersing optical element such as a prism or grating is required in the echelle spectrometer. Since the publication of reference 10, a number of components in the AOTF-echelle spectrometer have been changed. In the current system, the detector is a Hamamatsu CCD (model HC230-1007). The polarizers are  $\lambda$ -BBO Glan-Taylor polarizers (Casix in USA). With these polarizers, a 90° separation of the polarized beams is achieved (rather than a 2° separation with the MgF<sub>2</sub> Rochon polarizers of the original system), so a more compact arrangement of the AOTF input optics is achieved. The AOTF in the current system is a quartz device designed by MVM Electronics. This AOTF provides the capability of multi-wavelength simultaneous operation, since a multi-frequency RF driver is incorporated into the system. This will allow for monitoring ICP emission signals from multiple elements simultaneously, unlike the original AOTF-echelle spectrometer, which provided single wavelength, rapid-sequential monitoring capabilities. The air-ICP data presented below was obtained for single-frequency operation of the MVM AOTF, at high RF drive power (5-10 Watts) using an RF synthesizer - power amplifier system. Preliminary data for multi-frequency operation, using the 3-frequency AOTF controller from MVM at low power (approximately 1 Watt, without the RF power amplifier incorporated into the system), is presented for a mercury lamp source.

### 2.4. Reduced-Pressure Air-ICP Operation

The continuous sampling air-ICP system is operated using a Plasma-Therm model HFL5000D, 40 MHz, 5-kW ICP system. A low-flow quartz ICP torch (Precision Glassblowing of Colorado) is used, to allow operation using air or argon as the plasma gas. This torch has a reduced outer annulus width (0.5 mm) compared to a standard ICP torch (1 mm). Operation of the ICP is initiated using argon as the plasma gas, with argon introduced into the gas inlet (shown in Figure 3). The Roots blower is set to a relatively low speed (approximately 440 rpm) and the sampling pump is turned off during ICP start-up.

After initiation of the argon plasma, the Roots blower speed is increased, so that argon and some air (drawn through the Teflon sampling chamber, which is open to room air on the inlet end) are introduced into the axial channel of the ICP. The RF power is increased from 1-kW to approximately 1.5-kW to sustain this argon-air plasma. At this point, the argon supply to the ICP plasma and auxiliary gas flows and to the gas inlet is gradually switched to air, and the RF power is increased from 1.5-kW to approximately 3-kW, as the argon plasma switches to an air plasma. After the switchover to air is complete, the plasma and auxiliary gas flow rates are adjusted to approximately 20 and 1.5 lpm of air, respectively. After the air-ICP is operating, the Roots blower speed is increased to approximately 1100 rpm, the gas inlet line is removed (and the inlet is capped), and the sampling pump is turned on. A valve on the inlet to the sampling pump and the speed of the Roots blower are adjusted so that proper gas sample flow rates through the Teflon sampling chamber and into the axial channel of the ICP torch are established. Gas flow rates of approximately 30 standard lpm and 1 standard lpm, through the sampling chamber and into the axial channel of the ICP, respectively, are used.

For laboratory testing of the continuous sampling air-ICP system, the sampling chamber was open on one end, so room air was drawn through the chamber and into the air-ICP. Aqueous solution standards of metals were introduced into a CETAC Technologies U5000-AT ultrasonic nebulizer, and the dry aerosol output from the nebulizer was connected to the port on the inlet side of the sampling chamber (nebulizer spike in Figure 3). This arrangement was used for introducing metal aerosols into the sampling chamber and the air-ICP system for calibration and monitoring experiments. For the laboratory testing described below, the sampling chamber was operated at room temperature, and the sampling probe and the 12' long heat-traced Teflon line were not connected to the sampling system.

### 3. Results and Discussion

#### 3.1. Laboratory Testing of the Continuous Sampling Air-ICP System

A limited amount of analytical laboratory data has been acquired using the continuous sampling air-ICP system at this point, due to the recent assembly of the Teflon sampling chamber and incorporation of the chamber with the reduced-pressure air-ICP system. The testing that has been done has focused on the detection of the metals As, Be, Cd, Cr, Hg, and Pb, introduced into the sampling chamber and air-ICP by nebulizing single-element solutions of the metals using an ultrasonic nebulizer. Optical emission signals from the metals introduced into the air-ICP have been detected using the AOTF-echelle spectrometer system, including acquiring spectral data, performing calibration experiments, and conducting time-scan and continuous monitoring tests.

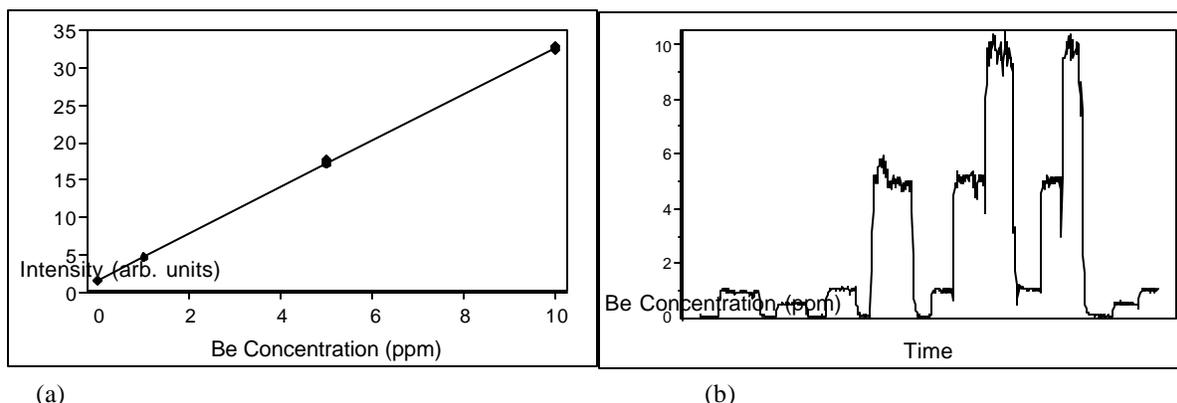


Figure 5. (a) Calibration curve obtained for the Be (II) 313.04-nm emission line, obtained by nebulizing solutions containing 0, 1, 5, and 10 ppm beryllium. (b) Plot showing continuous monitoring of the Be (II) 313.04-nm line, for solutions containing 0, 0.5, 1, 5, and 10 ppm beryllium.

An example of the calibration and continuous monitoring experiments performed is shown in Figure 5, for beryllium. Figure 5(a) is a calibration curve generated for the Be (II) 313.04-nm emission line. This calibration curve was obtained by introducing solution standards containing 0, 1, 5, and 10 ppm Be into the ultrasonic nebulizer, with the aerosol from the nebulizer introduced into the port (nebulizer spike) on the inlet side of the sampling chamber. Figure 5(b) is a plot showing continuous monitoring of the Be (II) 313.04-nm emission line, performed after calibration. This data was obtained by nebulizing solutions containing 0, 0.5, 1, 5, and 10 ppm Be, over a period of time in excess of 30 minutes (1000 data

points at a signal integration time of 2-s per point). The values in Figure 5 are the solution concentrations, introduced into the ultrasonic nebulizer, not the aerosol concentrations introduced into the air-ICP. Based on the solution flow rate to the nebulizer (1 mL/min), the approximate nebulizer efficiency (12.5% assumed, based on a previous measurement), and the gas flow rates through the nebulizer (1 lpm) and the sampling chamber (30 lpm), the approximate aerosol concentrations for 1, 5, and 10 ppm solution concentrations are 4, 20, and 40  $\mu\text{g/dscm}$ , respectively.

The signal stability for the beryllium monitoring data shown in Figure 5 is approximately 2-5% relative standard deviation, for the time periods that beryllium was introduced into the sampling chamber and air-ICP (the signal plateaus in Figure 5(b)). Some of the source of this signal variation may be attributed to minor fluctuations in the primary and secondary sample flow rates due to pressure fluctuations caused by the sampling pump and Roots blower. However, additional sources of drift and signal variation may be attributed to variations in the air supply gas pressure (the laboratory building air supply was used directly, with no additional pressure regulation) and to variations in the RF power output of the ICP generator (a decades-old ICP system). The initial signal spike in the first 5-ppm Be monitor data shown in Figure 5(b) is believed to be due to an increase in the RF power output of the ICP generator. A detection limit of 0.04 ppm Be (approximately 0.16  $\mu\text{g/dscm}$ ) is obtained from the beryllium monitor data, by dividing three times the standard deviation of the blank (0 ppm Be introduced in Figure 5(b)) by the slope of the calibration curve. Detection limits for a number of other metals introduced into the reduced-pressure air-ICP using this sampling system were obtained during the course of the initial laboratory testing, by performing time-scan monitoring of ICP emission signals. Detection limits of approximately 12, 4, 200, and 80  $\mu\text{g/dscm}$  for chromium (Cr (II) 283.56 nm), manganese (Mn (II) 260.57 nm), mercury (Hg (I) 253.65 nm) and lead (Pb (I) 405.78 nm), respectively, were obtained. These detection limits are about the same as those obtained previously for the air-ICP and AOTF-echelle spectrometer system.<sup>10</sup> Detection limits for arsenic and cadmium are poorer than those reported previously, due to the low output power of the AOTF RF synthesizer-amplifier system at wavelengths less than 235 nm, the region of the strongest emission lines for As and Cd.

Preliminary data has been obtained for the multi-frequency AOTF – echelle spectrometer, using the 3-frequency RF driver from MVM Electronics. An example is shown in Figure 6, for a mercury pen lamp as the source. For this spectrum, the AOTF drive frequencies were set to select Hg lines at 313, 365, and 405 nm. At 313 nm, the Hg doublet (lines at 313.155 and 313.184 nm) is resolved; the Hg 312.57-nm line is also observed, since this line is within the optical bandpass of the AOTF. Similarly, at 365 nm, two lines (365.02 and 365.48 nm) are observed since they are both within the AOTF bandpass. The Hg lines at 313, 365, and 405 nm are from different orders of the echelle grating and appear at different positions on the CCD detector, as determined by the dispersion of the grating. Therefore, the Hg 404.66-nm line appears at a lower pixel number than the 313-nm lines and the 365-nm lines do. Within a given order of the echelle grating (for the 312.57, 313.155 and 313.184 nm lines, for instance), the standard increasing pixel number, increasing wavelength orientation of lines is observed. However, lines from different orders of the echelle grating appear at different spatial positions at the detector, as shown in Figure 6.

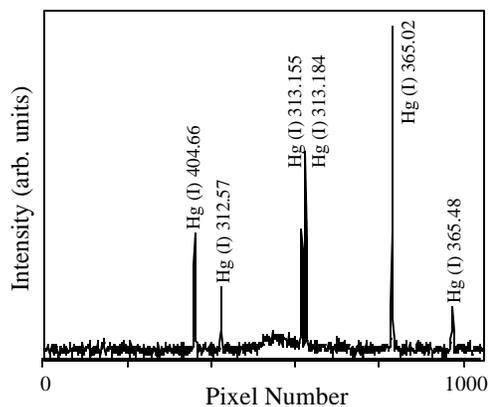


Figure 6. Mercury-line spectrum, obtained using the multi-frequency AOTF – echelle spectrometer.

### 3.2. Testing at DIAL

In the near future (prior to presentation of this work at the SPIE conference in September 1999), the continuous sampling air-ICP system will be tested at the Diagnostic Instrumentation and Analysis Laboratory (DIAL) at Mississippi State University. These tests will be performed on the combustion test stand at DIAL, a fuel oil-air furnace with capabilities for air preheating, introduction of fly ash mixed with the fuel, and introduction of heavy metal aerosols in the exhaust line.

The air-ICP CEM sampling probe will be installed in a vertical section of the exhaust line, several feet downstream in the water-cooled exhaust line where the off-gases will have cooled to below 200 °C, to protect the Teflon components in the sampling system. Data and samples will be collected under a variety of conditions, including blank runs, and runs where 75 and 25 µg/dscm of Be, Cd, Cr, Pb, and Hg will be added to the exhaust. These runs will be at least 2 hours in duration. During these runs, EPA Method 29 will be used to collect samples<sup>11</sup> that will be analyzed at a certified laboratory. Method 29 sampling will occur at a port in the pipe across from the sampling port for the air-ICP CEM in order to minimize differences between sample concentrations due to drop out of particles and particle segregation. These tests are intended to verify the compliance of this CEM with EPA relative accuracy requirements.

## 4. Conclusions

A continuous sampling air-ICP system has been designed for monitoring metals as a continuous emission monitor (CEM). The system consists of an air plasma that is operated inside a metal enclosure at a pressure slightly less than atmospheric pressure, using a Roots blower to draw sample continuously into the air-ICP. A Teflon chamber has been designed to allow continuous sampling of metal aerosols from an exhaust stack or process line for introduction into the plasma, from which optical emission from the metals in the sampled gas stream can be continuously monitored using a spectrometer system such as the AOTF-echelle spectrometer. The initial laboratory testing of this continuous sampling air-ICP system has shown the functional requirements necessary for the system to operate as a CEM. Additional laboratory and stack monitoring tests will be performed in the near future to more fully characterize the capabilities of the system for CEM applications.

## 5. Acknowledgments

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