ON-LINE, MULTIELEMENT ICP SPECTROMETER FOR APPLICATION TO HIGH TEMPERATURE AND PRESSURE FOSSIL FUEL PROCESS STREAMS

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KEYWORDS: ICP, On-Line Analysis, Fossil Fuel Analysis

ABSTRACT: METC is developing a real-time, multielement ICP spectrometer system for application to high temperature and high pressure fossil fuel process streams. The ICP torch operates on a mixture of argon and helium with a conventional annular swirl flow plasma gas, no auxiliary gas, and a conventional sample stream injection through the base of the plasma flame. The base of the torch body is a unique design, allowing process gas at 650°C to be injected into the torch. The RF generator (40.68 MHz) can deliver 10 kW, but the best detection limits have been observed at 5 kW. The detection system is a quartz fiber optic bundle mated to a battery of one-tenth meter monochromators with photomultiplier tubes. A microcomputer controls scanning of the monochromators and data acquisition from the PMTs. The METC ICP system is modular and mobile, allowing the system to be operated in close proximity to any process of interest.

Rising concerns about the potential release of harmful elements into the environment from coal utilization have driven the development of new analytical capabilities. Especially useful to the suite of advanced technologies under development by the Morgantown Energy Technology Center, (METC), would be a process monitor to perform real-time, multi-element trace analysis in a high temperature and high pressure environment. The inductively coupled plasma (ICP) spectrometer has the potential to perform this kind of process monitoring.

The role of the inductively coupled plasma, (ICP) as a process stream monitor for trace elements is only beginning to be realized, although it has been widely used for a number of years as a spectrometric emission source in elemental analysis laboratories. Previous work by other researchers [1] focused on monitoring of liquid phase process streams and looked only at elements at a relatively high concentration. Process monitoring by ICP spectrometry under conditions relevant to METC's advanced technologies has not been previously reported. The principle reason for this lack of progress is the difficulty of sustaining a stable plasma discharge around a high flow of carbon-containing sample gas.

Conventional ICP systems cannot operate at sample flow rates greater that two liters per minute, nor do they operate well with carbon-containing gases in the sample stream. The low flow requirements limit the use of an ICP argon plasma with particle-laden process streams, since at such low rates particles drop out of the gas stream before reaching the torch. Also, ICP plasmas quench when the carbon-containing gases of fossil fuel process streams are introduced, especially at high flow rates. Our torch design using a mixed gas plasma provides for operation at higher sample flow rates and for stable performance when analyzing samples of varied gas composition.

Prior work sponsored by METC, [2] was only partially successful in achieving this goal. On-line ICP analysis was attempted on a cleaned sample stream from METC's 107 cm diameter, (42 inch) fixed bed gasifier. An extracted gas stream was diluted with argon to 10% and introduced to the ICP torch at a flow rate of 1 l/min. Higher concentrations of gasifier gas extinguished the plasma, as did higher flow rates. The detection limits of this configuration were very poor. Consequently, METC began seeking methods that allow higher sample flow rates and concentrations while maintaining stable plasma conditions.

The conventional ICP excitation source is a plasma sustained at atmospheric pressure by coupling 27.12 MHz radio frequency power to a stream of argon. Almost all ICP systems use argon as the discharge medium, with aqueous solutions of unknowns nebulized into an argon sample stream injected into the argon plasma. This arrangement works well for power levels below 3 or 4 kilowatts, and for low flow sample streams that contain only argon and a small amount of aqueous aerosol.

Figure 1 shows METC's version of an ICP torch and the induction coil that transmits the high frequency power a radio frequency generator to the plasma. Similar to a conventional torch, it differs in some details because of the need to sustain a discharge with a high flow rate of carbon-containing gases in the sample stream. Also, the sample stream, coming from an industrial gasifier or combustor, is expected to vary widely in composition and particle loading on a timescale of seconds.

The torch uses conventional annular plasma gas injection. Auxiliary gas is not needed, and no provision for it is made in this design. The base of the torch is an unconventional construction, rather than the usual teflon, so a hot, high pressure sample line can be directly connected to the torch. The samples line can be maintained at an elevated (process) temperature to protect sample integrity by preventing tar condensation and particle dropout from loss of velocity. The sample injection tube is ceramic, and connects directly to the sample line through a drilled out compression fitting on the base. Graphite ferrules seal the compression fitting. The sample injection tube does not touch any teflon parts, and water cooling in the brass base protects the O-ring and adjacent teflon sections.

The presence of particles and carbon-containing polyatomic gases in the sample stream requires a high minimal power to sustain a stable discharge. Especially so, since the flow rate of sample gas into the discharge must be high to minimize particle dropout. Operation of argon ICP discharges above three or four kilowatts is difficult because the torch overheats. Our earlier work [2] reported configuration factors very close to unity generate a stable discharge with an argon and helium mixed gas plasma, but more recent work has shown that unusually small configuration factors, near 0.8, work well and facilitate construction and adjustment of the torch. The mixed gas plasma can be used at up to ten kilowatts with a high flow rate of carbon-containing sample gas. Optimum detection limits were found at five kilowatts, and it is not difficult to sustain a stable discharge at this power level. It is also possible to operate with pure helium, but there is no advantage and it is more expensive.

A frequency of 40.68 MHz, (higher than the conventional 27.12 MHz) was chosen for this torch design so the skin depth in the plasma would be smaller. Hence the coupling of power to the discharge is confined to the outer edge of the plasma flame where it is minimally affected by variations in the properties of the injected sample stream.

The torchbox opens from both the top and front, and has dark glass observation windows on two sides. This arrangement greatly facilitates adjustment of the torch and load coil orientation. Two windows on the back side provide optical access for the detection system optics. There is a separate impedance matching network and a Tesla coil in a housing attached to the torchbox. By using screw latches on all the doors and maintaining clean conductive surfaces around the doors and windows, electromagnetic leakage is kept well below safe limits.

The detection system consists of a battery of six one-tenth meter monochromators equipped with photomultiplier tubes. Each monochromator is equipped with a 3600 or 4800 groove/mm diffraction grating optimized for a particular region of the spectrum. The monochromators are all computer controlled, scanned via stepper motor drivers. Two of the eight monochromators are equipped with a red and near infrared sensitive photomultiplier tube, the rest are equipped with an ultraviolet and visible sensitive photomultiplier tube. Photomultiplier tubes were chosen for their excellent sensitivity and dynamic range. Their principle drawback is the need for separate monochromators for each detector, hence the battery of monochromators. Using two different types of photomultipliers also necessitates two independent high voltage supplies. The photocurrent from the photomultiplier tubes is connected to an A/D card in a PC, where the voltage developed across a load resistor is digitized and stored for processing.

The six monochromators are mounted on a platform adjacent to the ICP torch. Light from the plasma is gathered by two f/2, 5 cm diameter quartz lenses and focused into two 3mm diameter quartz fiber optic bundles. Each bundle is randomly split into four branches, and one branch is mounted at the entrance slit of each monochromator. The divergence angle of light from the quartz fiber is such that the gratings are nearly exactly filled without any optic between the bundle output and the entrance slit. The photomultiplier tubes are bolted directly over the exit slit of the monochromators.

For purposes of calibration, an aerosol from standard aqueous solutions is injected into the torch sample stream. The aerosol is generated with an ultrasonic nebulizer, which is much more efficient than the common Babington type aerosol generator. The aqueous aerosol is passed vertically through a drying oven to remove all water from the aerosol, and then through a chiller section, which condenses and removes most of the water vapor from the gas flow. Then the dry aerosol is directed through the sample line into the ICP torch. Overall efficiency of the generator is better than 80%.

A single software package to control the monochromators, acquire the data, and to calculate concentrations was written in C by a resident programmer. When the system is started and a new wavelength calibration is needed, the operator uses a low pressure mercury lamp to generate a known spectrum. The software knows approximately where to drive the stepper motors for various mercury lines; it positions the monochromator wavelength near a mercury emission line and acquires a spectrum of that region. Then the software executes a peak search routine and recalibrates its wavelength exactly.

When the system is to be operated, the first task facing the operator is calibration of both wavelength and concentration. Wavelength calibration was described above; concentration calibration is done conventionally, by supplying standard solutions over a range of concentrations and calculating a calibration curve. To measure concentration the software moves the monochromator wavelength to the peak region and acquires data over a small region of the spectrum. Before and after the measurement, the software moves the monochromator wavelength to either side of the line to acquire a background intensity, and calculates the area of the background trapezoid. It requires approximately one-half hour to start up the system and go through a complete calibration routine. Calibrations are reliable for periods of eight hours or longer. Real-time data are collected at one kilohertz and digitally processed to remove artifacts, and then summed and stored at the rate of one data point per second.

One of the principle requirements of our on-line system was that it be readily adaptable to use in the field. This meant that the system had to be modular and mobile. The torchbox, detection system, and calibration system must all be located at the sampling site, since preservation of sample integrity requires that the length of sampling tube be as short as possible. On the other hand, there is no requirement that the radio frequency generator be close at hand, since power can be conducted over tens of meters of coaxial cable without undue difficult or expense. Also, in many industrial process installations, the site where the sample is extracted is off-limits to personnel when the process is operating, and therefore all the controls and the computer must be remotely located. Figure 2 illustrates the various ICP modules.

The radio frequency generator is contained in a standard 19-inch cabinet, approximately two meters tall. The generator uses vacuum tubes for both stages of amplification and for the oscillator; the final stage is a single tube. This tube is very large and requires a large cooling air flow. Also, the separate vacuum tube stages require their own plate voltage, and therefore the power transformer is large and bulky. For these reasons, this unit is large, and until solid state technology advances, there is no prospect of obtaining a smaller one. There is a small, mobile transformer from which it is powered; the transformer takes 480 volts from a standard welding power receptacle and steps it down to 208 volts to operate the generator. This is convenient, since virtually all industrial facilities are equipped with 480 volt power. The generator also contains a full set of controls for power delivery.

The calibration rig is housed in a two meter high standard 19-inch rack, including the ultrasonic nebulizer, drying oven, cooling jacket, cooler, power supplies, and controllers. All these devices operate from standard low current 110 volt power.

Typically, the computer that runs the monochromators, and the radio frequency power generator are located near each other, so that data acquisition and processing and power delivery are controlled from one location. Additional power controls are located underneath the torchbox to facilitate starting and calibrating the system prior to making measurements on unknowns.

The plasma gas is a mixture of helium and argon. The argon is usually delivered from a large liquid argon tank. Helium is delivered from cylinders on a manifold or from a liquid helium tank. The tanks and cylinders are connected via mass flow controllers and can be remotely located, either near the computer and RF generator or at another convenient location.

Future plans for this instrument include field testing on coal combustors and gasifiers, refinement of torch design to increase reliability and minimize maintenance, and development of a CCD array detection system.

References

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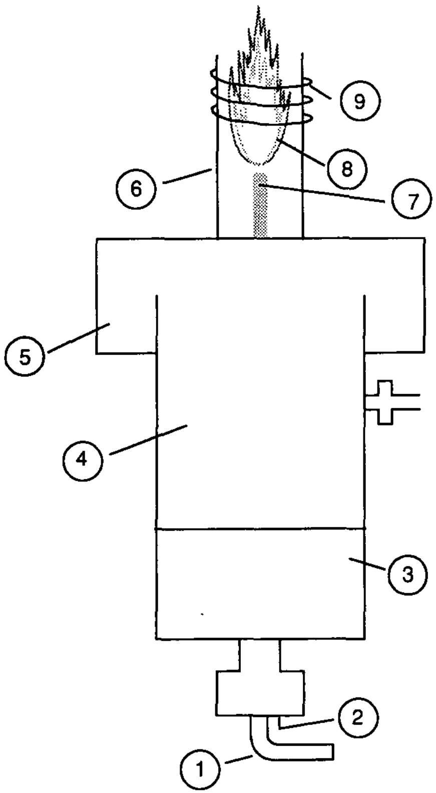

1. Heated Sample Line
2. Compression Fitting
3. Base Section
4. Teflon Body
5. Teflon Nut
6. Quartz Tube
7. Ceramic Sample Injection Tube
8. Plasma "Flame"
9. Copper Tubing RF Load Coil

Figure 1. ICP Torch with Load Coil and Plasma "Flame"

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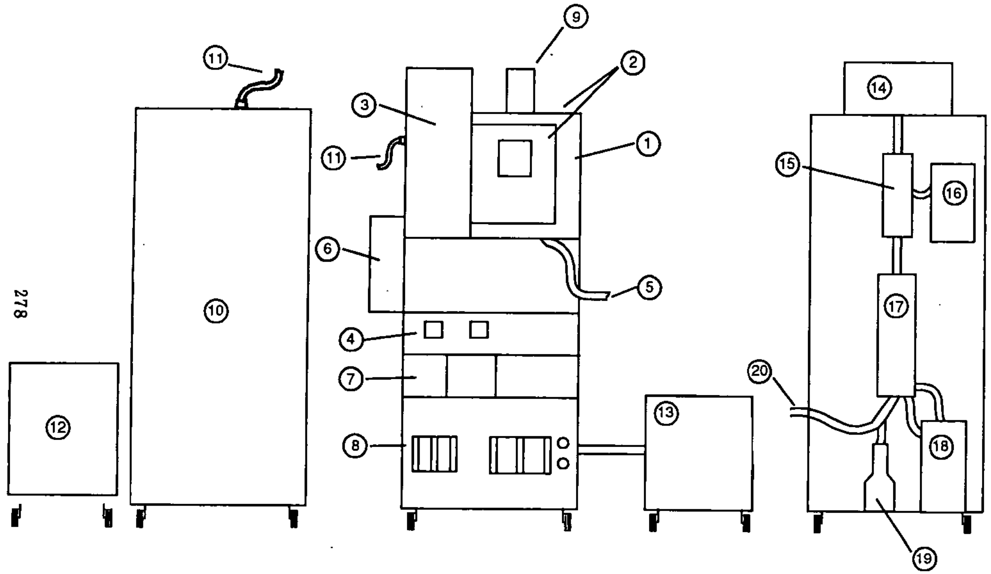

1. Torch Box
2. Access doors
3. Matching Network
4. Matching Network Control Panel
5. Heated Sample Line
6. Emergency Shutoff Control Box
7. Electronic Flow Controls and HV Power Supplies
8. Rotameters and Pressures Gauges
9. Chimney
10. 10 kW Radio Frequency Generator
11. Coax RF Power Cable
12. Mobile 480V to 208V Transformer
13. Chilled Water for ICP Load Coil
14. Ultrasonic Nebulizer, Standard Solution, and Peristaltic Pump
15. 500 °C Heater
16. Power Controller to Heater
17. 0 °C Condensor
18. 0 °C Chiller
19. Containment Vessel for Condensed Water
20. Sample Line to ICP Torch

Figure 2. Modular Arrangement of METC's Complete On Line ICP System

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