

## DEVELOPMENT OF ON-LINE GC/MS MONITORING TECHNIQUES FOR HIGH PRESSURE FUEL CONVERSION PROCESSES

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### INTRODUCTION

It is well known that on-line analytical methods offer considerable advantages over conventional off-line procedures for fuel conversion processes. Although many on-line spectroscopic detection systems for thermal process reactors have been reported [1-10], they have had only very little application to high pressure reactors [8-10]. Therefore, relatively little is known about the precise pathways and intermediate products involved in high pressure reactions. The application of real time, on-line chromatographic and/or spectroscopic techniques capable of throwing light on these processes is hampered by the high temperatures and pressures inside the reactor which complicate direct interfacing to standard analytical instruments.

As shown in previous work, thermogravimetry (TG) can provide detailed information on thermally driven conversion reactions, especially when combined with on-line detection and identification techniques such as Fourier transform infrared spectroscopy (FTIR) [1-7] and mass spectrometry (MS) [6,7]. However, high pressure TG systems have only recently become available for studying the basic pyrolysis and especially hydrolysis reactions involved in coal liquefaction, thus, the combined chromatographic/spectroscopic interfaces for such high pressure systems are only now producing results [11]. Other high pressure reactors of interest include those used to study the thermal processes in liquid fuels or in solvent based coal conversion. Thus there have been recent reports of on-line GC/MS monitoring of a high pressure recirculating autoclave used to study coal derived liquid model compounds [10]. Other work in our laboratory has examined the supercritical pyrolytic degradation of jet fuels with on-line GC/IR/MS [9]. Several of these systems have involved the use of a patented [12] automated vapor sampling (AVS) inlet [13] with short column or so called "transfer line" gas chromatography (TLGC) with MS [9-11] or FTIR [9].

This paper presents the experimental descriptions and results from three high pressure systems using a variety of components. The first is a high pressure TG/GC/MS system used to study coal hydrolysis. The other two use quartz tubing reactors to examine the liquid and gaseous products from the thermal decomposition of jet fuels.

### EXPERIMENTAL

**1. System I (thermogravimetry):** Figure 1 shows a schematic diagram of a high pressure thermogravimetric analysis system with on-line GC/MS. The system utilizes a CAHN TG-151 high pressure thermogravimetry (TG) instrument which operates at pressures up to 1000 psi with temperatures up to 1000 C at heating rates up to 25 C/min. The MS system is a mass selective

detector (MSD, HP 5871A) with a HP 9000 computer. The TG to MS interface consists of a 1 m long 50  $\mu\text{m}$  i.d. fused silica capillary, pressure reduction line for transferring vapor products at flows of 10-20 ml/min (at ambient pressure) to an automated vapor sampling (AVS) inlet developed at the University of Utah [12,13]. The AVS inlet performed pulsed sampling of the vapor product stream into a 2 m long, 150  $\mu\text{m}$  i.d., 0.12  $\mu\text{m}$  film thickness fused silica capillary (CP SIL-5CB, Chrompak) column directly connected to the MSD.

A 60 mg sample of coal was loaded into a specially-designed quartz crucible [11] and was placed in the high pressure TG. The TG system was purged with the reagent gases which were then set to their run flow ratio of 10:10:4 for the reagent gas, furnace flush gas and balance flush gas, respectively. The system was operated at 900 psi with  $\text{H}_2$  as the reagent gas and He for both flush gases. The total flow rate of the gases into the TG was adjusted to 1200 ml/min at ambient pressure. The pressure reduction line and AVS were heated to 200 C to minimize condensation losses, and the TLGC column was heated to 90 C for the analysis reported here. The TG and AVS-GC/MS systems were operated by two separate computers. Detailed parameters for the reactions (including systems II and III) are listed in Table 1.

**2. System II (continuous fluid flow reactor):** A similar pressure reduction capillary and AVS-GC/MS system have been used for a newly developed microscale quartz tube reactor for on-line liquid product analysis as shown in Figure 2. The continuous flow reactor consists of a 300 mm long, 2 mm i.d. quartz tube in a furnace with a uniform 150 mm long heated zone, which can be heated up to 1100 C at heating rates up to 50 C/min with the temperature measured both inside and outside the quartz chamber. The sample fluid flow can be precisely controlled at 0 to 5 ml/min at pressures up to 2000 psi using an HPLC pump (Milton Roy Co.). The pressure reduction line is a 1 m long, 25  $\mu\text{m}$  i.d. fused silica capillary with a volume flow of approximately 2  $\mu\text{l}/\text{min}$ . The filter frits and capillary are attached to the reactor to minimize the high pressure dead volume and minimally disturb the reaction process. The AVS-GC system used a 2 m long, 150  $\mu\text{m}$  i.d. fused silica capillary column (CP SIL-5CB) which could be temperature programmed from 30 to 280 C at heating rates up to 150 C/min. The GC column was directly coupled to a modified Ion Trap Mass Spectrometer (ITMS, Finnigan MAT) with tandem MS capabilities and electron ionization (EI) as well as chemical ionization (CI) options.

The sample solution was continuously pumped from a glass reservoir into the reactor at the chosen flow rate by the high pressure liquid pump. For experiments on the effect of dissolved oxygen during the thermal degradation, pure oxygen (or air) was bubbled via a 10  $\mu\text{m}$  porous filler in the sample reservoir, otherwise, pure nitrogen was bubbled to exclude oxygen. For some tests, a metal foil was inserted into the reactor from one end to serve as a catalyst. The reactor was pressurized to 1500 psi by adjusting the flow-splitting needle valve. The preheater was set at 250 C (590 F). Ten minutes after the reaction temperature was reached, the first AVS sample was taken and the GC temperature was programmed with an initial hold at 30 C for 5 min and then linearly heated to 250 C in 20 min for each vapor sample. The results of four or more repetitive samples were continuously recorded by a PC computer.

**3. System III (continuous fluid flow reactor with product phase separation):** Figure 3 shows the continuous flow reactor with on-line AVS-GC/MS for gaseous product analysis. Components which differ from system II include: a backpressure regulator (Grove Valve & Regulator Co. model 91W) which maintains the pressure in the reactor while conducting a mixed phase mass flow of 0 to 10 mg/min at ambient pressure; a gas-liquid separating device for the products; and

a Mettler AE 240 electronic micro balance system interfaced to a PC computer with ~ 40 g of weighing capacity and 0.1 mg accuracy. The AVS inlet was used on a Hewlett Packard 5890II Gas Chromatography system with a 10 m long, 530  $\mu\text{m}$  i.d. porous layer fused silica capillary column (GS-Q, J & W Scientific). The outlet of the column was connected via an open split interface and a 0.5 m long x 100  $\mu\text{m}$  i.d. capillary to an MSD (HP 5971A) with a 1993 HP Chemstation PC software system, which can scan from  $m/z$  1.2 to monitor  $\text{H}_2$ .

In order to focus our analytical attention on the smaller hydrocarbon products, eg.  $\text{C}_1$  through  $\text{C}_3$ , the reactor system was modified from that of Fig. 2 to that shown in Fig. 3. The experimental procedure was similar to system II except that the reactor's pressure was controlled by adjusting the controlling gas pressure to the backpressure regulator valve, and the continuous recording of liquid product weight. A one hour run was used for weight analysis while ten repetitive samples were taken for MS. The use of the MSD with its updated software enabled scanning a mass range to include hydrogen although its detection is not reported here.

## RESULTS AND DISCUSSION

**System I:** Fig. 4 shows high pressure TG/GC/MS data from the hydrolysis of a Blind Canyon, Utah coal in  $\text{H}_2$  at 900 psi. Fig 4(a) shows the thermogravimetry (TG) and first derivative of the TG (DTG) curves for the temperature range of 400 to 600 C at 10 C/min with a 5 min hold at the final temperature. The major weight loss process centered at 450-460 C to the main coal pyrolysis step in helium (He). The second DTG peak near 570 C was not obtained in runs in He (see related work in ref. 11). Fig. 4(b) shows a corresponding ion chromatogram for a phenolic fragment ion ( $m/z$  107) which indicates that alkylphenols are even greater abundance in the higher temperature process than in the main pyrolysis. The same selected ion is shown with an expanded time scale in Fig 4(c) to demonstrate the amount of isomer and homolog separation available on the short GC column; the o-cresol peak is partially resolved from the m- and p-isomers, and the dimethylphenols are largely separated from the ethylphenols.

**System II:** The total ion chromatograms (TICs) of a JP-7 jet fuel sample subjected at 1500 psi to different temperatures with a mean residence time of 2.0 min are presented in Fig. 5 for the 20 min temperature program runs. Since the unreacted jet fuel is composed of saturated straight chain and cyclic hydrocarbons, with from nine to sixteen carbons and traces of aromatics, its supercritical point is estimated to be at a temperature of 400 C (750 F) and a pressure of 250 psi. Under supercritical conditions the thermal decomposition products are dominated by short chain components. The results in Fig. 5 show that below the supercritical condition (77 F), no decomposition products were detected, while at higher temperatures (800 and 900 F), significant levels of  $\text{C}_2$  -  $\text{C}_7$  products were obtained and the quantity increased with the reaction temperature. To determine the influence of oxygen and catalysts during the thermal decomposition, oxygen, metal foil (~100  $\text{mm}^2$ ) and organic metal were added in separate experiments. Fig. 6 shows the various effects of oxygen, metal Cu and 1 ppm of Cu(II) 2,4-pentanedionate on the decomposition of JP-8 (all at the single temperature of 900 F). As seen in Fig. 6 the addition of oxygen and catalysts significantly increased the decomposition products ( $\text{C}_2$  -  $\text{C}_7$ ). Although in all of these preliminary experiments the objective was to demonstrate steady state reaction conditions, it can be seen that the complete fuel could be monitored for compositional changes from  $\text{C}_2$  to  $\text{C}_{17}$  with cycle times of 25 min or less.

**System III:** Fig. 7 shows the weights of the total liquid materials (sample plus liquid products) versus reaction time for JP-7 jet fuel decompositions (a) at different reaction temperatures and (b) its gas conversion with and without addition of methycyclohexane vs reaction temperature. Because methycyclohexane is a hydrogen donor, its addition to the JP-7 jet fuel produced the highest gas conversion. Fig. 8(a) illustrates the relative amount of the low molecular weight products such as methane, ethylene, ethane, propylene, and propane under the supercritical conditions. Fig 8(b) shows analysis of standard mixtures consisting of 25% methane, 25% ethylene, 25% propylene and 25% butylene.

## CONCLUSIONS

Fast, repetitive "transfer line" GC/MS (TLGC/MS) analysis of products from high pressure reactors by means of a heated capillary pressure reduction line is feasible provided compounds of interest are sufficiently volatile and stable. TLGC/MS analysis can be performed regardless of whether reactor contents are in the vapor, liquid or supercritical fluid phase or their mixtures. However, careful removal of particulate matter from the product stream is required to prevent plugging of the pressure reduction line.

Use of quartz tubing reactors reduced the possibility of catalytic effects from the walls of the reaction vessel and made it easier to visually observe the reaction processes and residue formation in the reaction chamber compared to other systems (such as stainless steel tubing reactors or autoclaves). The high pressure TG/AVS-GC/MS system reliably handled solid samples in reactive atmospheres with simultaneous sample weight and evolved gas product GC/MS monitoring. The newly developed, on-line quartz-reactor AVS-GC/MS systems for high pressure reactions continuously handled gaseous, liquid, and supercritical liquid samples reliably. The system II sampling interface was efficient for high molecular weight (liquid and supercritical liquid) product analysis. The system III interface was sufficient for low molecular weight (gases) product analysis and was demonstrated here with continuous monitoring of the sample weight conversion. Therefore, the newly developed systems represent a significant improvement over conventional off-line methods and should facilitate elucidation of the mechanisms and kinetics of fuel conversion processes.

## ACKNOWLEDGEMENTS

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**TABLE 1: EXPERIMENTAL CONDITIONS**

Conditions	System I	System II	System III
1. Sample	Blind Canyon coal in hydrogen	JP-7 & JP-8 jet fuel	JP-7 jet fuel
2. Reactor	high pressure thermobalance CAHN model TG-151 temp: ambient to 1000 C	quartz tube flow through reactor with catalytic inserts; temp: ambient to 1100 C; residence time: 1 sec to 5 min	quartz tube flow through reactor with catalytic inserts; (with a micro-balance)
3. Pressure reduction line	900 psi → ambient 1 m x 0.050 mm fused silica cap.	1500 psi → ambient 1 m x 0.025 mm fused silica cap.	1000 psi → ambient backpressure regulator
4. Vapor sampling inlet	120 C; pulse: 500 ms at 75 sec intervals	250 C; pulse: 800 ms at 25 min intervals	40 C; pulse: 400 ms at 2 min intervals
5. Transfer line GC column	2 m x 0.150 mm Me-silicone 0.12 μm 90 C isothermal	2 m x 0.150 mm Me-silicone 0.12 μm 30-200 @ 15 C/min	10 m x 0.530 mm Porous large cap. 40 C isothermal
6. Detector	quadrupole mass spectrometer- model HP 5971 (Hewlett-Packard) with a HP 9000 computer	Miniaturized Ion Trap Mass Spectrometer (Finnigan-MAT) with a PC computer	quadrupole mass spectrometer- model HP 5971 (Hewlett-Packard) with a PC computer
7. Mass range	m/z 10 ~ 300	m/z 10 ~ 500	m/z 1.2 ~ 80

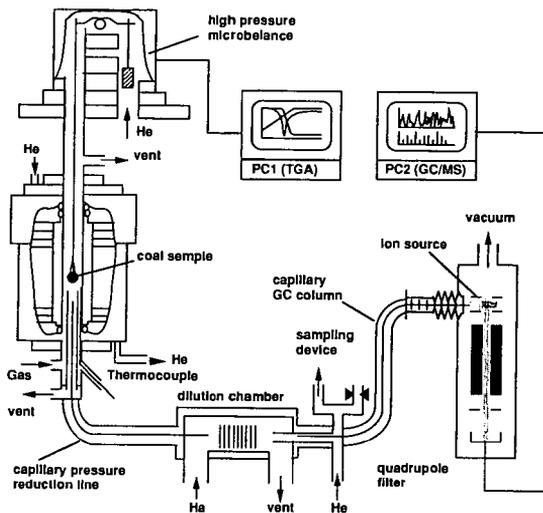


Figure 1. High pressure TG/GC/MS system (system I)

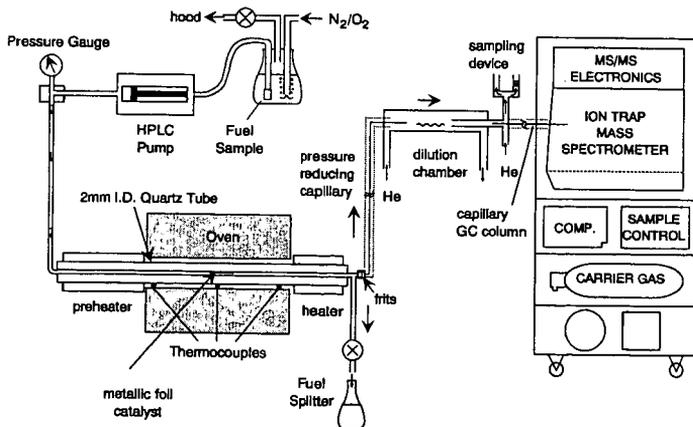


Figure 2. On-line GC/MS monitoring of high pressure fluid, flow-through reactor (system II)

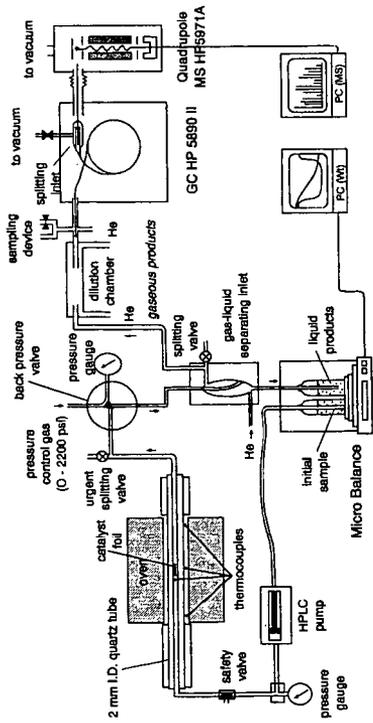
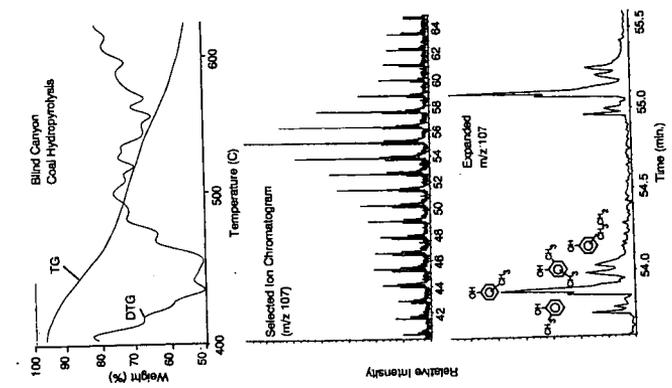


Figure 3. On-line GC/MS monitoring of high pressure fluid, flow-through reactor with product phase separation (system III).

Figure 4. Partial TG/GC/MS data from the analysis of the Blind Canyon, Utah coal in H<sub>2</sub> (900 psi, 10 °C/min) showing the detailed monitoring of alkylphenols in the evolved gases.

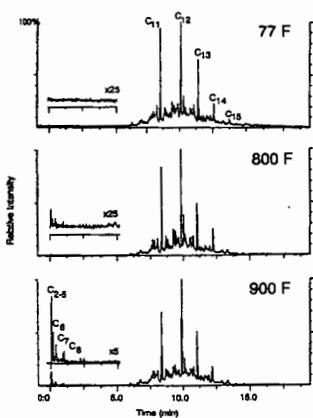


Figure 5. Effect of reaction temperature on the thermal decomposition of JP-7 jet fuel under supercritical conditions (1500 psi) in a 2 mm i.d. quartz tube flow-through reactor, system II (residence time 2.0 min).

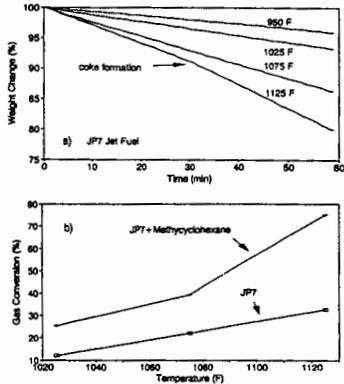


Figure 7. Effect of reaction temperature on (a) the weight change of liquid sample plus liquid product and on (b) the gas conversion of supercritical thermal decomposition of JP-7 jet fuel (1000 psi, < 1.5 min residence time).

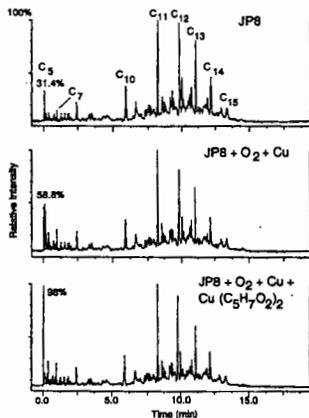


Figure 6. Effect of catalysts on the thermal decomposition of JP-8 jet fuel in system II under supercritical conditions (1500 psi, 900 F, 2.0 min residence time).

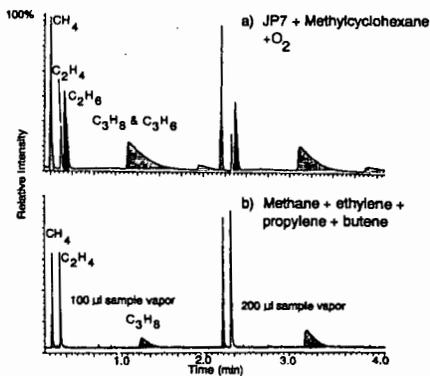


Figure 8. GC/MS profiles of (a) gaseous thermal products of supercritical thermal decomposition of JP-7 jet fuel (1000 psi, 1000F, < 1.5 min residence time) and (b) standard compounds (25% for each of methane, ethylene, propylene and butene).

## SENSOR TECHNOLOGY FOR ADVANCED COMBUSTION CONTROL AND MONITORING INSTRUMENTATION

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KEYWORDS: GAS SENSORS, COMBUSTION CONTROLLER, EMISSIONS MONITORS

### ABSTRACT

With increasingly stringent environmental legislation, there is a growing need for low cost instrumentation for combustion control and emissions monitoring. While low cost is necessary, advanced instrumentation also must be simple to operate and calibrate, require minimum maintenance, and give stable, reliable data. Combustion of fossil fuels leads to formation of CO, NO<sub>x</sub>, SO<sub>2</sub>, and other pollutants depending on the fuel and the combustion conditions. We will describe catalytic heat flux sensor technology and instrumentation based on these sensors for the quantitative measurement of CO, NO<sub>x</sub>, and SO<sub>2</sub>. Various strategies for control of emissions and for maximum fuel efficiency based on these measurements will be discussed.

### INTRODUCTION

The 1990 Amendments Act of the Clean Air Act require tighter control of the emissions released during the combustion of fossil fuels. The new legislation is now targeting small industrial and commercial size combustion processes such as heaters, boilers, and stationary IC engines. Continuous Emissions Monitoring (CEM) systems capable of monitoring the major fossil fuel combustion emissions, NO<sub>x</sub>, SO<sub>2</sub>, and CO, have been used for over ten years on utility size boilers and large gas turbines. However, the prohibitively high cost of these systems, as much as \$150,000, is too high of an expense burden for smaller combustion processes. Sonoxco has developed a line of sensors to measure the stack gas levels of NO<sub>x</sub>, SO<sub>2</sub>, and CO on coal-, oil-, and gas-fired processes. The sensors are low cost and easily configurable into monitoring and control instrumentation to provide continuous measurement and control of these gases.

### SENSING METHODOLOGY

The Sonoxco CO, NO<sub>x</sub>, and SO<sub>2</sub> sensors are catalytic heat flux devices. Each sensor is comprised of two temperature sensitive elements, one active and the second a reference. The active element is coated with a highly selective catalyst that promotes an exothermic reaction of the component to be measured. The temperature difference between the active and reference elements is directly proportional to the gas concentration. As an example, the CO sensor operates by catalyzing the reaction of CO with oxygen as follows:



Resistance temperature detectors (RTD) are used for the temperature measuring elements for the three sensors. Because the RTD resistance is proportional to temperature, the corresponding difference in resistance between the active and reference elements is linear with gas concentration. A bridge circuit can be used to produce a 0-5 Vdc signal that is directly proportional to the gas concentration as shown in Figures 1 and 2 for the CO and NOx sensors. The SO<sub>2</sub> sensor signal is also very linear with changes in SO<sub>2</sub> concentration [1]. The designs of the NOx, CO, and SO<sub>2</sub> sensors are identical with the exception of the proprietary active catalyst coatings. The Sonoxco sensor configuration is shown in Figure 3.

Catalytic heat flux type sensors have been used commercially for decades primarily for LEL (Lower Explosion Limit) applications. What distinguishes our sensors from the other heat flux sensors and from sensors using different sensing methodologies such as electrochemical are; 1) high sensitivity, the CO and NOx sensors have sensitivities on the order of 5 ppm, the SO<sub>2</sub> sensor about 20 ppm, 2) high selectivity towards the measuring gas, and 3) long sensor life even in harsh applications such as coal-fired processes.

#### CO SENSOR FOR MAXIMUM FUEL EFFICIENCY

Combustion efficiencies vary with air/fuel ratio. At low excess air levels incomplete combustion lowers efficiency while at high air/fuel ratios, energy is wasted by heating the unused air. In theory optimum combustion control efficiency can be achieved by monitoring either oxygen or CO and controlling the air/fuel ratio. In practice using both CO and oxygen provides better control of the combustion process efficiency than using either component alone [2]. An example of such a system utilizing both CO and oxygen measurements for control is the Bailey Controls ICCS (Industrial Combustion Control System). The ICCS unit uses a ZrO<sub>2</sub> solid electrolyte oxygen sensor and the Sonoxco CO sensor. The ICCS system is closed-coupled mounted to the stack eliminating costly heat traced sample lines. In addition, both the oxygen and CO sensors operate at temperatures above the dew point of the process gas and as a consequence water is not removed from the sample gas prior to measurement. This greatly simplifies the design of the sampling system bringing significant savings in the overall cost of the system. The ICCS system sells for \$4200, a cost that can be paid for from the fuel savings in a few years even on small industrial combustion processes.

#### SENSOR ARRAY FOR COMBUSTION AND NO<sub>x</sub> CONTROL

The overall simplicity and compatibility of the Sonoxco CO, NO<sub>x</sub>, and SO<sub>2</sub> sensors make the sensors particularly suited for sensor array networks. By combining the signal information from each of the array sensors the effect of sample condition variability, such as changes in sample flow and temperature, may be distinguished from real changes in gas concentration. The array can also be used to correct for cross-interferences from the other gas components on each individual sensor.

Sonoxco is currently working on a program funded by the Gas Research Institute to develop a sensor array for natural gas combustion control systems. The array is comprised of the Sonoxco CO and NO<sub>x</sub> sensor, and a ZrO<sub>2</sub> solid electrolyte sensor provided by another OEM sensor manufacturer. Presently the sensor array algorithms are being evaluated using a test apparatus

that simulates the conditions of a real gas-fired process. Later in the program, control strategies will be developed to use the sensor array to control combustion efficiency and NO<sub>x</sub> emissions from gas-fired processes. The control system is intended to be a low cost system applicable to small industrial and commercial size combustion processes. A preliminary design of the system utilizes a closed-coupled mounting of the sensor array to the stack with the unconditioned sample gas drawn directly over the sensors via an air-driven aspirator or sample vacuum pump. Conditioned sensor signals are then transmitted serially to the controller housed in a separate enclosure. The inherent simplicity of the system combined with such features as auto calibration should provide a system requiring minimum maintenance and operator intervention.

The control system can use the NO<sub>x</sub> measurement in a closed-loop with an EGR (Exhaust Gas Recirculation) valve to control NO<sub>x</sub> levels, or alternatively to meter the quantity of steam injected in water/steam injection systems used to lower flame temperatures to reduce NO<sub>x</sub> emissions. The system can also be used on large combustion processes as feed forward or feed back control to NO<sub>x</sub> reduction systems such as SCR (Selective Catalytic Reduction).

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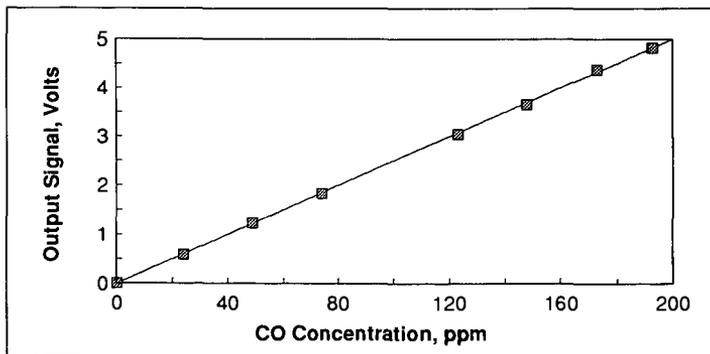


Figure 1. Signal linearity of the Sonoxco CO sensor.

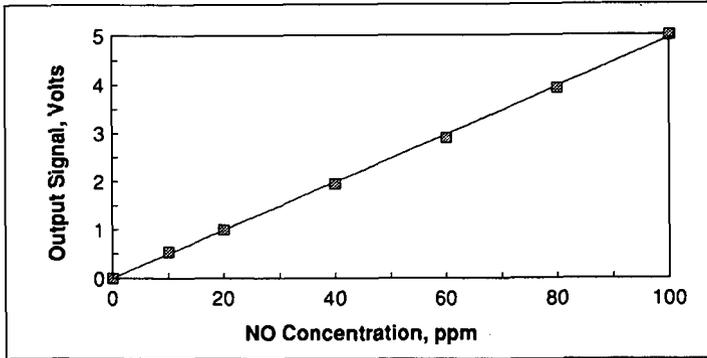


Figure 2. Signal linearity of the Sonoxco NOx sensor.

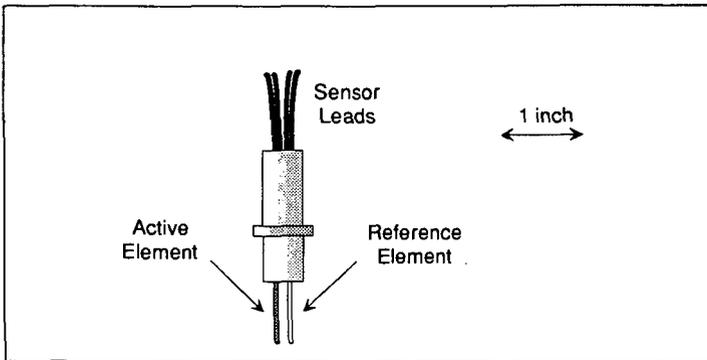


Figure 3. Sonoxco CO, NOx, and SO<sub>2</sub> sensor configuration.

## ON-LINE FT-IR ANALYSIS OF FOSSIL-FUEL FIRED POWER PLANTS

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### ABSTRACT

This paper describes the test of a prototype FT-IR CEM system at a full scale power plant. Initial tests were done in an extractive mode over a one week period and measured SO<sub>2</sub> levels were compared to levels measured by an existing CEM system. The system was able to report concentrations of six different gas species simultaneously, and IR spectra were periodically saved for future analysis and measurement of other gas species concentrations. Subsequent tests will involve a comparison of simultaneous in-situ and extractive measurements with FT-IR based CEM systems and a long duration (one-month) evaluation of the extractive system.

### INTRODUCTION

The use of an FT-IR based continuous emission monitoring (CEM) instrument for a fossil-fuel fired power plant offers several advantages: 1) it can be used in either an in-situ (emission/transmission) or extractive (transmission) mode; 2) FT-IR transmission spectroscopy can measure concentrations for multiple gas species which significantly reduces the cost and complexity of the measurement system; 3) FT-IR emission/transmission spectroscopy allows the determination of concentration and temperature information on gases and number density, size, temperature and composition information on particles; 4) FT-IR transmission spectroscopy can provide concentration measurements on species which are difficult to provide by other on-line techniques (e.g. NH<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>). Although FT-IR is an established multicomponent sensor technology, the use of FT-IR for CEM systems is still under development [1]. FT-IR has been used for both in situ and extractive monitoring of coal combustion, pulp and paper mills, and hazardous waste incinerators [2,3,4,5]. This paper describes extractive FT-IR measurements were performed at Cogentrix of Richmond, Richmond, VA.

### RESULTS AND DISCUSSION

Description of Test Site - The first field test was conducted from May 24-27, 1993 at the Cogentrix Coal-Fired cogeneration plant in Richmond VA. The plant consists of eight spreader stoker-fired boilers rated at 300k lbm/hr. Two boilers are joined to one turbine with a maximum expected generator output of 55 MW each. The plant also supplies process steam for a nearby chemical production facility. The Cogentrix power plant uses a urea injection system to control NO<sub>x</sub> and reduce SO<sub>2</sub>, and also uses lime spray drying and additional capture in the baghouse resulting in 90% reduction in SO<sub>x</sub> emissions.

Samples were extracted from the process after urea injection, but prior to particulate collection or SO<sub>2</sub> removal, with the STI Dilution Probe (Graseby/STI, Waldron, AR). The majority of samples were obtained with a dry basis probe (a heat exchanger is used to condense water prior to sample dilution), although some samples were obtained with a wet basis probe (no heat exchanger), and sampling was performed with and without a glass fiber filter. The process gas was diluted ≈20:1 with instrument air (CO<sub>2</sub>-free, dry air) before being transferred to a 5.6 m effective path-length gas cell through a 100' long, 1/4" PTFE transfer line. Figure 1 is a schematic of the sampling probe and monitoring system. The FT-IR spectrometer was a Bomem MB100 equipped with a liquid N<sub>2</sub> cooled, MCT detector. All spectra were obtained with 1 cm<sup>-1</sup> spectral resolution, and the cell temperature and pressure were maintained at 30° C and 1 atm respectively. Pure component spectra were measured in the laboratory for CO<sub>2</sub> (from 424.1 to 50000 ppm), CO (from 0.56 to 10000 ppm), NO (0.85 ppm), and SO<sub>2</sub> (0.85 ppm) under similar conditions. Theoretical, high resolution (< 0.0625 cm<sup>-1</sup>) spectra were

generated from the HITRAN Optical Spectroscopy Database using USF HITRAN-PC (University of South Florida Research Foundation, Tampa, FL) for CO<sub>2</sub> (from 12.5 ppm to 1250 ppm), H<sub>2</sub>O (from 100 to 10000 ppm), NH<sub>3</sub> (from 0.125 to 12.5 ppm), HCl (from 0.25 to 25 ppm), NO (from 1 to 100 ppm), and SO<sub>2</sub> (from 1 to 100 ppm). The high resolution spectra were deresolved to 1 cm<sup>-1</sup> using a triangle apodization function to approximate the instrument line shape for the Bomem MB100 spectrometer.

**Gas Analysis** - Prior to analyzing gases extracted through the dilution probe, a calibration gas (a mixture of 251 ppm NO, 635 ppm SO<sub>2</sub>, 205 ppm CO, and 5% CO<sub>2</sub> in N<sub>2</sub>) was measured directly and also measured after being diluted 20:1 with N<sub>2</sub>, to verify the optical pathlength and gas flow meters, respectively. The optical pathlength was measured as 5.6 ± 0.1 m. The same calibration standard was used to measure the dilution ratio for the STI probe. The ratio was determined to be ≈20:1. For continuous measurements, single beam spectra were recorded at ≈1 min intervals (25 full scans at 1 cm<sup>-1</sup>), absorbance spectra were calculated based on a previously recorded reference spectrum, gas concentrations were determined using a modified principal component regression, and concentration vs. time was reported for six gas species.

The FT-IR based continuous monitor measured process gas concentrations for approximately three hours from 18:00 hours to 21:00 hours on May 25, 1993. Figures 2 and 3 compare CO<sub>2</sub> and SO<sub>2</sub> levels, respectively, as measured by the FT-IR system to those measured by the existing CEM. The FT-IR-based CO<sub>2</sub> levels were calculated using a laboratory measured CO<sub>2</sub> spectrum as the reference and a previously determined calibration curve. The existing process monitor does not measure CO<sub>2</sub> directly, but the CO<sub>2</sub> concentration can be inferred from the process stoichiometry and the measured O<sub>2</sub> concentration. The FT-IR-based SO<sub>2</sub> levels were calculated using a HITRAN-PC generated reference, while the existing CEM uses a fluorescence measurement. The reported values for the existing CEM system are 15 min averages for the period in question, while the FT-IR data represent 1 min averages. Calibrations based upon laboratory pure-component spectra and upon theoretically generated pure component spectra worked equally well for calculating process concentrations. The periodic spikes in the concentration measurements correspond to blow-back periods, periods when instrument air is forced back through the probe and through the heat exchanger to remove particulates and condensed H<sub>2</sub>O. The timing of blow-backs could be varied from 15 min to 1 hour or could be controlled manually. In future tests, the timing will be controlled by the FT-IR system computer.

**Trace Gases** - The FT-IR system was also able to detect CO and NO at levels of 72 and 150 ppm, respectively. The 20:1 dilution in the probe resulted in single digit ppm concentrations in the gas cell for these species. The current continuous analysis software was not able to accurately quantify these gases due to baseline anomalies and interference by remaining water (even with the heat exchanger, residual water levels approached 1000 ppm in the cell, partly from incomplete drying of the instrument air used for dilution). This problem is being addressed in software which is under development.

Because of the urea injection, ammonia is expected to be present in the effluent in addition to the standard combustion gases expected from coal. Sulfur dioxide and ammonia react in hot combustion gases to form particulates. This precipitation is both temperature and moisture sensitive, and can cause difficulties when trying to measure SO<sub>2</sub> and NH<sub>3</sub> in an extracted gas stream [1]. The concentration of NH<sub>3</sub> was first measured from a calibration standard (25.4 ppm NH<sub>3</sub> in N<sub>2</sub>) that was injected through the dilution probe. All of the gas lines leading to the probe were pressurized with the calibration gas for 8 hours prior to the experiment to condition the lines. Without prior conditioning, NH<sub>3</sub> continues to permeate the teflon tubing and accurate NH<sub>3</sub> concentrations are not obtained. When the calibration gas was injected through the filter, no detectable NH<sub>3</sub> (<0.1 ppm) made it through the probe into the gas cell after 20 min. It is possible that residual water in the glass filter and heat exchanger was absorbing the NH<sub>3</sub>. If the calibration gas was allowed to bypass the glass fiber filter and the heat exchanger, the NH<sub>3</sub> concentration in the gas cell increased to > 1 ppm (vs. 1.27 ppm expected).

Figure 4 presents the NH<sub>3</sub> concentration vs. time over a one hour time period. After 1 min of time elapsed, 25.4 ppm NH<sub>3</sub> was injected into the dilution probe (with the filter removed, and heat exchanger bypassed). The continuous FT-IR monitor measured an increase in NH<sub>3</sub> concentration to 10 ppm where it leveled off. At 16 minutes, instrument air was forced through the probe, and the extraction was switched from cal gas to process gas. After an initial increase in NH<sub>3</sub> concentration that corresponded to the blow-back, the NH<sub>3</sub> concentration

dropped to zero. After 15 min, the process was switched back to the NH<sub>3</sub> calibration standard, but the NH<sub>3</sub> levels in the cell did not recover during the duration of the analysis. A second series of experiments was performed with a 47 ppm NH<sub>3</sub> standard with similar results. Preliminary measurements with the cal gas reported increasing levels of NH<sub>3</sub>. Upon switching to the process gas, the level of NH<sub>3</sub> dropped to zero and ≈ 1 hour of cal gas flow was required before NH<sub>3</sub> levels returned to normal. During process gas sampling, a powdery substance quickly coats the inside of the sample probe and, if the filter is removed, the lines leading to the educator assembly. This substance is probably a combination of ammonium sulfates, sulfites, and ash. It is possible that the moist particulates which line the tubing after sampling process gas continue to absorb NH<sub>3</sub> from the calibration standards until saturated. This absorption would account for the extremely long lag times required for NH<sub>3</sub> from the calibration standard to reach the FT-IR system after sampling process gas.

Similar experiments were performed with HCl calibration standards. Although HCl was easily detected during dilution experiments performed directly into the gas cell, when the HCl calibration standard (≈ 50 ppm HCl in N<sub>2</sub>) was injected through the wet-basis probe (no heat exchanger) with filter, the HCl concentration increased to ≈ 1 ppm in the gas cell after prolonged flow (> 20 min). It is possible that moisture trapped in the filter from the ambient air was absorbing some of the HCl. Upon switching to process gas, no HCl was detected in the cell (< 0.2 ppm) and upon switching back to the calibration gas, no HCl was detected after 60 min. Again, it is possible that moisture and particulates from the process stream are collecting in the filter and tubing and absorbing/reacting with the HCl. Removal of the glass fiber filter did not increase the level of HCl measured in the process.

#### FUTURE PLANS

The objective of this work is to develop in situ and extractive FT-IR monitors for emission monitoring and process control. Future field work will address some of the problems discovered during extractive measurements of NH<sub>3</sub> and HCl, and will include in situ monitoring as well.

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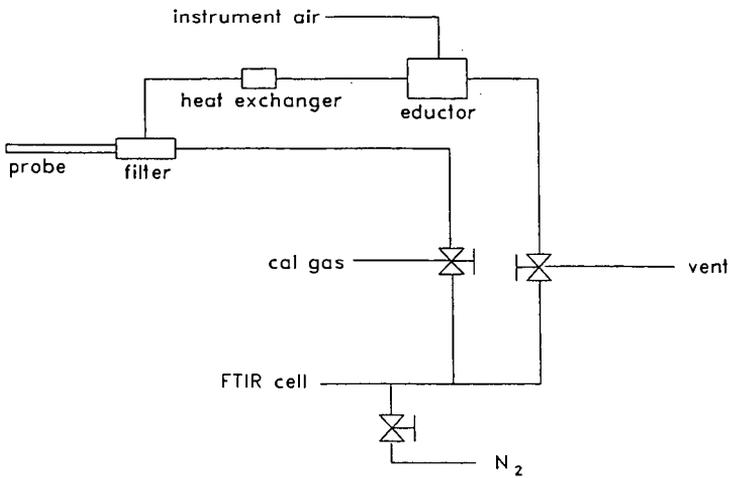


Figure 1. Schematic flow diagram for dilution probe.

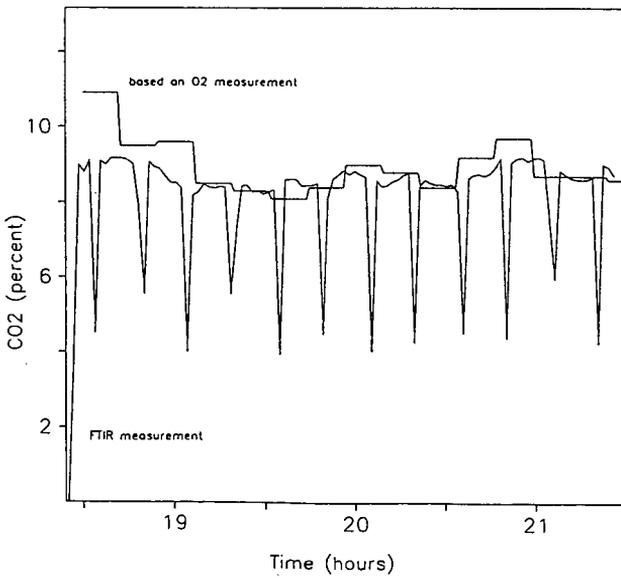


Figure 2. Comparison of CO<sub>2</sub> concentrations as measured by continuous FTIR system and as inferred from O<sub>2</sub> measurements.

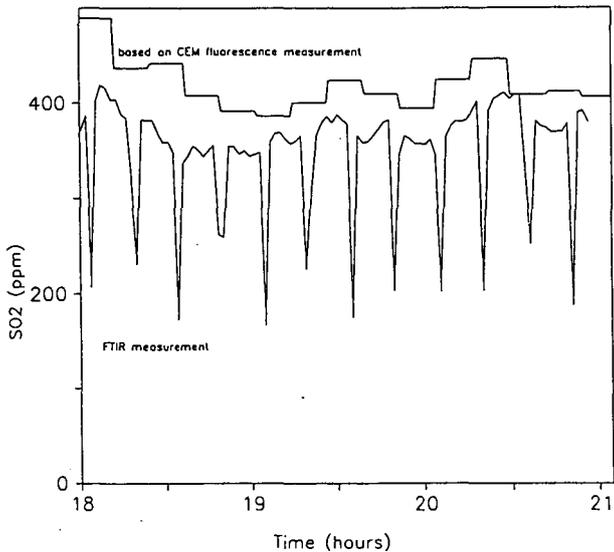


Figure 3. Comparison of SO<sub>2</sub> concentrations as measured by continuous FTIR system and as measured by existing fluorescence monitor.

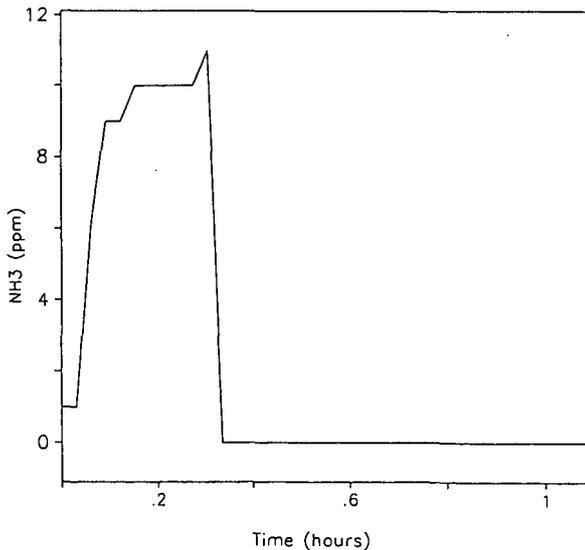


Figure 4. Continuous NH<sub>3</sub> measurements during cycling of standard calibration gas and process gas streams.

**IMPROVED PLASMA TORCH AND DATA ANALYSIS SOFTWARE FOR AN ON-LINE,  
MULTIELEMENT ICP SPECTROMETER DESIGNED FOR APPLICATION TO HIGH  
TEMPERATURE AND PRESSURE FOSSIL FUEL PROCESS STREAMS**

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**KEY WORDS:** ICP, On-Line Analysis, Fossil Fuel Analysis, Artificial Neural Networks

**ABSTRACT:** METC is continuing to improve its 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. A new, demountable torch design comprised of three ceramic sections allows bolts passing the length of the torch to compress a double O-ring seal. This improves the reliability of the torch. A battery of monochromators, controlled by a microcomputer, is the detection system. In lieu of conventional data reduction techniques, a neural net analysis of emission spectra is being developed to analyze the data.

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. Some details of METC's efforts in this direction have been reported previously [1]. The raison d'etre of METC's ICP work is to address process monitoring under conditions relevant to METC's advanced fossil fuel technologies.

The shortcomings of conventional ICP systems plumbed directly to high temperature and pressure process systems have been previously discussed [1]. In brief, these systems cannot sustain a plasma in a gas stream containing a large proportion of molecular gases, they cannot be connected to hot, pressurized sample lines, and the plasma emission spectrum contains strong interfering molecular bands. Our previously reported torch design solved these problems, but suffered from a tendency for the plasma to erode some of the O-rings after several hours of operation. These o-ring seals eroded because they tended to develop leaks. They developed leaks because they were not compressed, and were sealed only by forcing the quartz auxiliary tube into the torch, without additional compression. Also, the brass base of the old torch design spanned several centimeters between the electrically hot side of the radio frequency (RF) coil and the chassis ground. This tended to aggravate the tendency of the plasma to discharge back into the torch towards ground. We have developed a new torch which is sectioned into several pieces. By running bolts through the length of the torch, all the o-ring seals in it can be compressed by tightening the bolts. The new torch will be made of an insulating ceramic capable of direct connection to a hot sample line, but which also minimizes the tendency of the discharge to follow plasma gas leaks towards ground. Also, the design protects some of the O-rings by providing water cooling between the O-rings and the hotter parts of the torch.

The detection system has previously been described [1]. In a typical experiment, integrated line intensities from the emission spectrum of an element of interest are recorded from solutions of known concentration nebulized into the sample gas stream, and a calibration curve is drawn to relate element concentration to integrated intensity. Although this established approach works well for simple systems, the ICP optical emission from a fossil fuel sample stream is very complex, is influenced by the presence of easily ionized elements, and has a variable and noisy background. Given the limitations of present curve fitting algorithms and other methods of ICP analysis it was desired that a "better" way to determine elemental concentration was needed; a method that could account for the interferences and complications present in these spectra.

It was decided that an Artificial Neural Network (ANN) might be a very powerful tool in analyzing this data. ANNs have become very popular in recent years in applications of pattern recognition, speech recognition and other areas due to their adaptability to different types of data. ANNs were inspired by and function similarly to biological neural networks.

Figure 1 shows a typical Back Propagation neural network architecture. This particular architecture is the one used for the METC ICP application i.e. two layers and one output. Data values ranging from 0 to 1 enter the network at the input layer one point per node. Each of these values is then multiplied by the hidden weights and summed at the hidden layer nodes. These values are then multiplied by the output weights and are summed at the output node(s).

Training the network entails first gathering training data representative of a pattern of known, experimental inputs and outputs, i.e. known concentrations and integrated line intensities. The data could include the intensities of several emission lines from one element, the intensities of lines of easily ionized elements, lines from elements that overlap the emission lines of elements of interest, background spectral regions, molecular emission band intensities, and even ancillary data on experimental conditions, such as flow rates, RF power level, etc. Given the training data input, the network adapts and adjusts until its calculated output becomes very close to the output values of the training data. Once trained, unknown input data may be entered and the network will generate an answer based on the data for which it was trained. Back propagation neural networks function well in pattern recognition and classification, but are often very slow to train if large, i.e. if they contain a large number of inputs and/or hidden neurons.

The back propagation neural network used for the METC ICP is a commonly used, general network architecture. The uniqueness of its application to the ICP system derives from knowledge of which peaks to use to give a good representation of the concentrations of the elements. Background noise and interactions between elements play a large part in determining which peaks to use since the number of inputs (data points) needs to be minimal, for reasonable computational times, but must be large enough to give the network information sufficient to make reliable predictions.

Initial experiments with the neural net were performed by generating data with a mercury pen lamp or an iron hollow cathode lamp. Using neutral density filters, training data of intensity versus filter attenuation was generated. Several emission lines and a background region were included in the data set. It was found that the neural net works well over a decade of data, but did not work well over a larger range. Some experiments with data from the actual ICP system were also performed, with promising results. Efforts to further develop the neural net continue.

The new torch design was constructed in teflon and operated on argon and argon and helium mixtures. Improved reliability was found under a variety of operating conditions. The new design also provides for adjustments of the alignment of the plasma, auxiliary, and sample gas tubes. Planned work includes constructing a ceramic version and operating with hot sample gas input.

#### References

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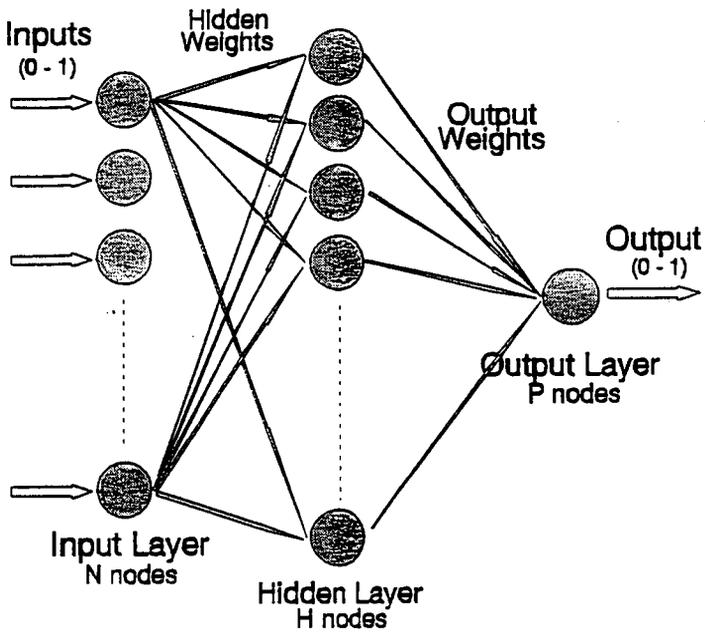


Figure 1. Input, Hidden, and Output Layers of an Artificial Neural Network.