

Continuous Monitoring of Hazardous Smokestack Metal Emissions Using Inductively Coupled Argon Plasma Atomic Emission Spectrometry

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Introduction

Emission of hazardous air pollutant metals from the smokestacks of boilers, incinerators, and furnaces has become a matter of significant environmental concern and the object of increased regulatory scrutiny. At issue, is the ability of large-scale combustors such as these to maintain operation in compliance with the regulatory restrictions put in place to safeguard the public from the health and environmental risks associated with airborne metal pollutants. Until recently, the only available means of demonstrating compliance involved periodic stack testing to determine, under a given set of operating conditions, the average rates of emission of the offending metals. While the available stack testing methods appear to provide reliable measurements of stack gas metal concentrations *at the time of sample collection*, there has been no provision for interim or continuous compliance assurance. For many gaseous pollutants, continuous emissions monitors (CEMs) have been available for decades and are extremely effective for documenting day-to-day emissions and alerting operators in the event of non-compliant operation. A similar capability for monitoring metal emissions has in the past, not been available. However, as a result of a successful research and development effort, and a program of iterative testing and engineering refinement, the analytical performance and practicality of a prototype multimetals CEM has been demonstrated to a satisfactory degree.

The technology in question was developed as a result of a collaboration between a U.S. Navy laboratory and the U.S. Army ordnance demilitarization community. While the original intent of this system was to provide compliance assurance monitoring and to facilitate process control for numerous munitions deactivation furnaces, the technology has proven to be extremely versatile and has demonstrated operational compatibility with other large-scale combustors such as hazardous waste incinerators and coal-fired boilers. The multimetals continuous emissions monitor, known as the TraceAIR, is capable of rapid and simultaneous detection of all 14 metals designated as hazardous air pollutants by the U.S. EPA, plus virtually any metal in the chemical periodic table. Detection sensitivity is superior to all competing technologies and is more than adequate to fulfill compliance assurance monitoring requirements.

Specific details of the design and operation of the TraceAIR multimetals CEM can be found elsewhere [1], but are summarized in the present paper in order to include a number of recently-implemented engineering refinements. The system, as presently configured, continuously extracts a representative stream of stack gas using a revolutionary shrouded probe design [2] and transports that stream through a heated conduit to the elemental analyzer, in this case, an inductively coupled argon plasma spectrometer. A patented sampling interface [1,3] introduces precise aliquots of the sample stack gas into the argon plasma at approximately 63 second intervals. For each individual aliquot, concentration measurements are made for all metals simultaneously, using a technique called atomic emission spectrometry. Operation of the entire system, including calibration and quality control procedures, is executed automatically under computer control.

While the potential of the multimetals CEM for providing compliance assurance has been clearly evident for some time, demonstrating the accuracy capabilities of this system has been problematic. The present size and complexity of the ICAP elemental analyzer used in this prototype system have prohibited the convenient and desirable location of the analyzer immediately adjacent to the smokestack. Therefore, as a matter of necessity, the technique has relied to a large extent on the pneumatic transport of extracted gases and entrained particulate matter from the stack to the analyzer. This feature, as originally configured and practiced, proved to be a considerable liability, but has since performed more satisfactorily as a result of several refinements.

The results of preliminary performance testing of the TraceAIR multimetals CEM revealed a significant measurement bias that suggested possible problems concerning sample transport inefficiency. Subsequent systematic investigation of aerosol deposition losses in the sample extraction and transport components indicated the existence of serious operational deficiencies to which the noted measurement bias could be attributed with a high degree of certainty. In order to resolve these deficiencies, a detailed assessment of the existing sample extraction and transport hardware and methodology was undertaken, involving the use of a valuable computational tool for modeling aerosol deposition losses in sampling probes and conduits [4]. This approach not only provided theoretical evidence to corroborate the inadequate performance of the existing sampling hardware and methodology, but also proved useful in facilitating the design of an improved sampling system. The present paper discusses the design of the improved sampling system and its integration into the TraceAIR multimetals CEM system, and the results of initial field evaluations.

Principle of Operation

At the heart of the TraceAIR multimetals CEM is the elemental analyzer consisting of an inductively coupled argon plasma (ICAP) spectrometer (Thermo Jarrell Ash, Franklin, MA), custom-modified to accept a stream of sample stack gas for on-line analysis. ICAP instruments are more traditionally used for laboratory analysis of metals in liquid samples such as wastewater. However, airborne metals entering the high-temperature argon plasma are subject to the same processes of vaporization, excitation, and ionization as metals introduced in the form of aqueous solutions. Following excitation, each individual metal element emits a “fingerprint” spectrum of light, the intensity of which corresponds to the concentration of each metal element in the sample. A multichannel, direct-reading optical spectrometer disperses these emissions according to wavelength and a series of dedicated photodetectors intercepts and records the individual light emissions. Because the argon plasma is a nearly ideal atomization and excitation source, even in the presence of injected stack gas, remarkable detection sensitivity is achieved for the hazardous air pollutant metals. These metals include Ag, As, Ba, Be, Cd, Co, Cr, Hg, Mn, Ni, Pb, Sb, Se, and Tl. The TraceAIR multimetals CEM is calibrated using precision-generated aerosols of known metal composition and concentration. Metal-containing aerosols of an identical nature are used for calibration drift measurements. The ICAP elemental analyzer makes automatic corrections for spectral interferences arising from concomitant metals and molecular species, as well as performing a subtraction procedure for contributions from the plasma spectral background. All airborne metal concentrations are normalized to standard conditions, and as an option, can be also normalized to 7 percent oxygen using data acquired from an on-line diluent oxygen analyzer.

In order for the high-performance elemental analyzer to be useful, it is necessary to extract a stream of sample stack gas and transport it to the ICAP instrument. Formerly, this extraction was accomplished using a sampling probe similar to that used in EPA Method 29, equipped with a “shepherd’s crook” isokinetic sampling nozzle. Stack gas was extracted using flow rates that were constantly adjusted, according to changing stack velocities, in order to maintain isokinetic sampling conditions. The probe was attached to the CEM elemental analyzer using a 15.2 meter long, 10 mm inner diameter teflon sample line, thermostatted to a temperature of approximately 110 °C. Occasionally, a 22.8 meter long sample line was used, as the installation required. A sampling interface, consisting of a series of solenoid valves and a length of tubing (sample loop), was used to accommodate differences between the relatively high and often variable flow rates required to support isokinetic sampling, and the low, and necessarily constant flow rates required for plasma sample introduction. While stack gas was continuously extracted and transported to the sampling interface, sample aliquots of that stack gas were periodically delivered from the sample loop to the plasma. The block diagram shown in Figure 1 illustrates the sampling configuration described above.

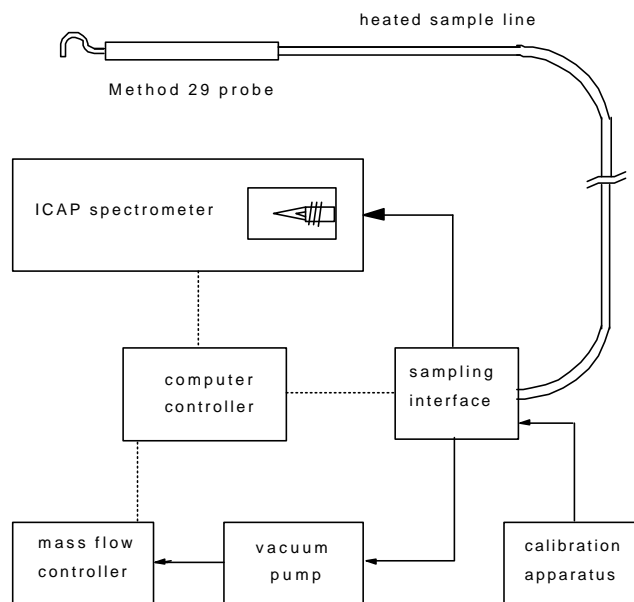


Figure 1. Block diagram of TraceAIR multimetals CEM as originally configured.

Sample Collection and Transport Considerations

A distinct disadvantage of the probe and isokinetic sampling nozzle assembly described above, is its propensity to accumulate sample aerosol residues due to the effects of turbulent gas flows at the nozzle opening, and inside the nozzle and probe. Experimental investigation of deposition losses in this hardware revealed that 40-50 percent of the total mass of sample aerosols traversing the nozzle and probe were lost in this manner. These losses were quantified by rinsing the probe and nozzle in the customary manner using a brush and a dilute nitric acid solution, followed by spectrochemical analysis of the rinseate. A similar approach, taken to determine the extent of deposition losses occurring specifically in the heated sample line, revealed deposition losses that accounted for up to 15 percent of the total mass of sample aerosols extracted. In numerous instances, the combined losses for the probe, nozzle, and sample line, almost

completely accounted for the measurement bias that was documented for the TraceAIR multimetals CEM when compared side by side with a reference test method such as EPA Method 29.

Further investigation of this problem, using the DEPOSITION Program [4], a computational tool developed to predict the transport behavior of airborne particulate matter, yielded results that implied that deposition losses in the sampling system described above, were exacerbated by the small size of the isokinetic sampling nozzle opening, the tortuous path followed by the sample aerosols through the “shepherd’s crook” nozzle, and the length, number of bends, and the predominantly horizontal orientation of the heated sample line used in previous testing.

The intent of the original sampling system design was to emulate some of the proven features of EPA Method 29, *i.e.*, isokinetic sampling using a similar probe and nozzle. However, the fact that EPA Method 29 must rely on a careful post-test probe wash procedure to recover and quantitatively account for deposited aerosols was overlooked during the design phase of the present developmental effort. Indeed, metal analyte residues recovered from Method 29 probe wash rinseates often constitute fractions in excess of 50 percent of the total sampling train catch [5]. Accordingly, the TraceAIR multimetals CEM, which does not include a practical provision for recovering deposited aerosols from the sampling system hardware, is at a constant disadvantage relative to EPA Method 29, which routinely recovers and quantitates the deposited fraction of sample aerosol as part of the total sample mass. This realization was sufficient to warrant consideration of an alternative design for the multimetals CEM sampling system, and a correspondingly improved sample collection and transport methodology. The goal of this effort

then, was to identify a sampling probe design that would ensure that aerosol deposition losses could be dramatically reduced relative that previously observed using the Method 29 probe arrangement. Similar requirements were established for the sample transport components. The anticipated outcome, therefore, would be to construct and demonstrate a sampling system for the TraceAIR multimetals CEM that would promote accurate measurement of extracted stack gas metal concentrations.

Shrouded Probe-based Sampling System

The shrouded sampling probe [2] was originally designed for an application that demanded efficient collection and transport of large (10 micron) particulates from a free stream of variable velocity, while operating the probe at a constant flow rate. Figure 2 illustrates the construction of the probe and shows the position of the sampling inlet in relation to the shroud. Working in concert with the conical sampling nozzle, the shroud, which vents through a restrictive opening at the rear, effectively reduces the velocity of the incident gas stream by as much as a factor of 3 relative to that of the free stream. Consequently, a much larger nozzle inlet opening can be used, compared to a conventional isokinetic probe operating in the same free stream at a given sampling flow rate. The shroud has a secondary advantage in that it allows the sampling inlet to intercept gases from a relatively quiescent region of flow along the central axis of the shroud. Anisokinetic effects and turbulent deposition at the probe opening are both minimized, contributing to both efficient aspiration of particulates and satisfactory particle throughput. In principle, the shrouded probe is designed to provide effective collection and throughput of airborne particulates while operating under conditions that are not necessarily isokinetic, but within which modest anisokinetic errors can be tolerated.

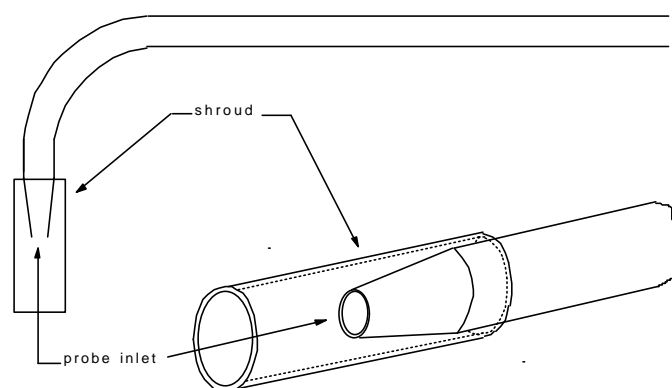


Figure 2. Schematic drawing of the shrouded probe.

All of these features make the shrouded probe very appealing for integration into the TraceAIR multimetals CEM sampling system. Accordingly, a commercially-available (Andersen Instruments, Smyrna, GA) shrouded probe, designed for constant-flow operation at 57 liters/min in a free stream velocity range of 5-20 meters/sec, was obtained. The shroud itself, has a diameter of 53 mm and a length of 106 mm. The sampling inlet opening is 18.2 mm. The shrouded probe was modified to include a thermostatted heating jacket and compression fitting assembly to facilitate mounting in a smokestack sampling port. A 6.1-meter long heated sample

line with a 28.7 mm I.D. teflon hose was selected to optimally transport the 57 liter/min sample gas stream extracted by the shrouded probe.

The preferred flow rate for optimum operation of the TraceAIR multimetals CEM sampling interface is approximately 15-16 liters/min. To accommodate the difference between this flow and that required for the shrouded probe, the sub-sampling extractor assembly illustrated in Figure 3 was devised. This assembly is connected at the terminus of the heated sample line in such an arrangement that the sub-sampling nozzle is inserted several centimeters inside the teflon sample conduit. A sub-sample of the extracted stack gas stream is thus collected, under isokinetic conditions, at the 15-16 liter/min flow rate described above. The 15-16 liter/min flow rate is established using the same vacuum pump and mass flow controller depicted in Figure 1. The balance of the 57 liter/min flow rate required for operation of the shrouded probe is established using a vacuum eductor, connected to the body of the sub-sampling extractor assembly as shown in Figure 3. The eductor, which contains a precision venturi, generates the necessary suction to achieve this flow rate when a stream of compressed, motive air is applied to the venturi inlet. The sub-sample extractor assembly is mounted immediately adjacent to the sampling interface inlet port in order to maximize the length of large-bore conduit traversed by the extracted stack gas. Both the vacuum eductor and vacuum pump/mass flow controller assemblies are adjusted according to stack gas conditions, to achieve the desired gas flow rate under actual conditions.

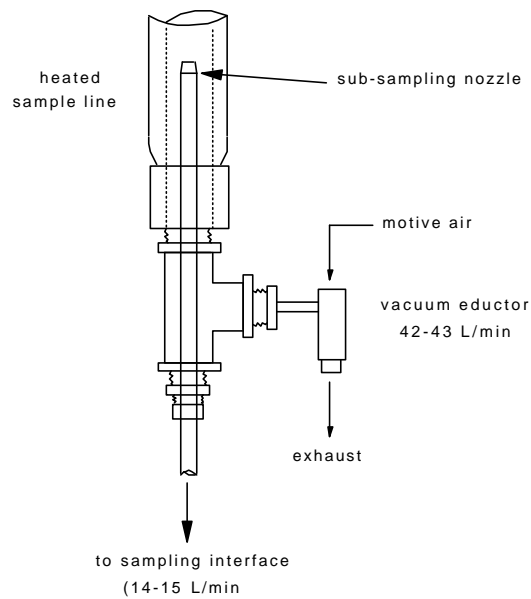


Figure 3. Sub-sample extractor assembly.

Initial Assessment of Shrouded Probe-based Sampling System

The TraceAIR multimetals CEM with the shrouded probe-based sampling system was set up to conduct stack gas emissions monitoring for an APE 1236 Munitions Deactivation Furnace, at Tooele Army Depot, Utah, operating in full production mode. The trailer containing the CEM instrumentation was located near the base of the 11-meter exhaust stack, with the shrouded probe mounted in a port located approximately 6 meters above the ground. This arrangement allowed the use of a 6.1-meter heated sample line with a 28.7 mm I.D. teflon hose. The relatively close proximity of the CEM trailer to the stack allowed the sample line to be installed in a nearly straight configuration with a significant incline. Sharp bends and horizontal sections that contributed to the detrimental operation of the previous sample line were thus eliminated. The initial assessment of the shrouded probe-based sampling system involved a series of trial

measurements during which Method 29 sampling trains were operated as a reference to allow calculation of the relative accuracy of the TraceAIR multimetals CEM. The results of the Method 29 measurements were not yet available at the time of writing the present paper. However, included below are examples of representative data recorded by the TraceAIR multimetals CEM during periods of furnace operation involving munitions waste introduction and during sessions involving artificial introduction of metal-containing aerosols into the furnace exhaust stream.

Metal Emissions Resulting from Munitions Deactivation

Figures 4-6 depict the emissions of lead (Pb), antimony (Sb), and barium (Ba), recorded by the multimetals CEM during furnace introduction of projectile primers. Metal concentrations are expressed in units of micrograms per dry standard cubic meter. Individual multi-element measurements were made at approximately 63 second intervals. Stack gas conditions were as follows: temperature, 96 °C; absolute pressure, 84.6 kPa; moisture, 6 percent. While the percussion primers were introduced into the rotary kiln at an approximate rate of 1200 per hour, random detonation of these items was responsible for the temporal emission behavior shown in Figures 4-6.

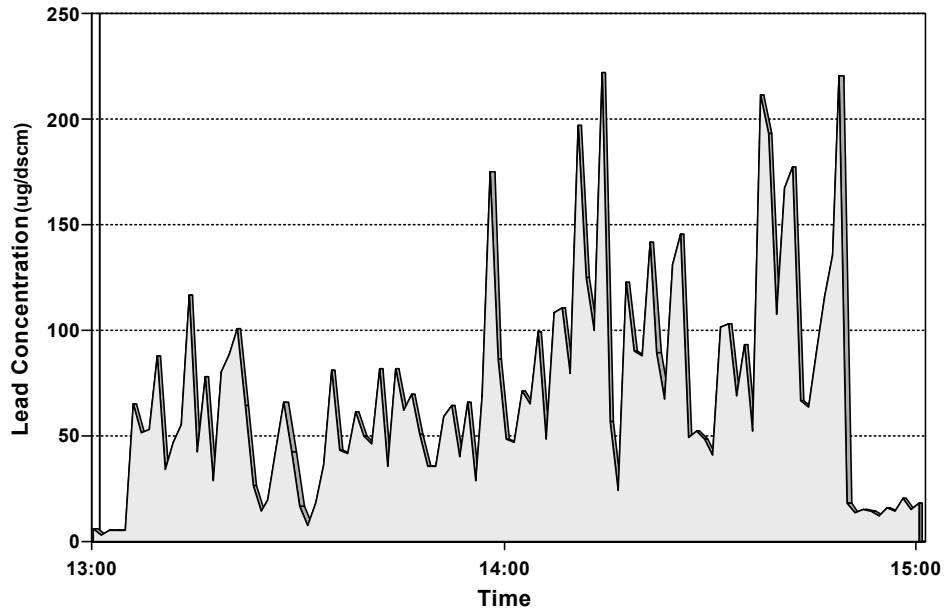


Figure 4. Lead emissions resulting from munitions deactivation

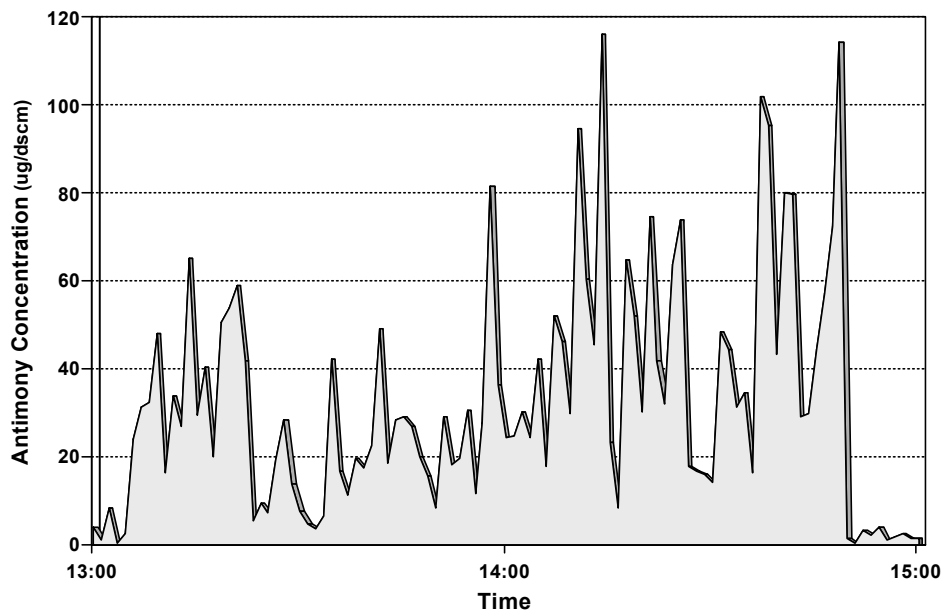


Figure 5. Antimony emissions resulting from munitions deactivation

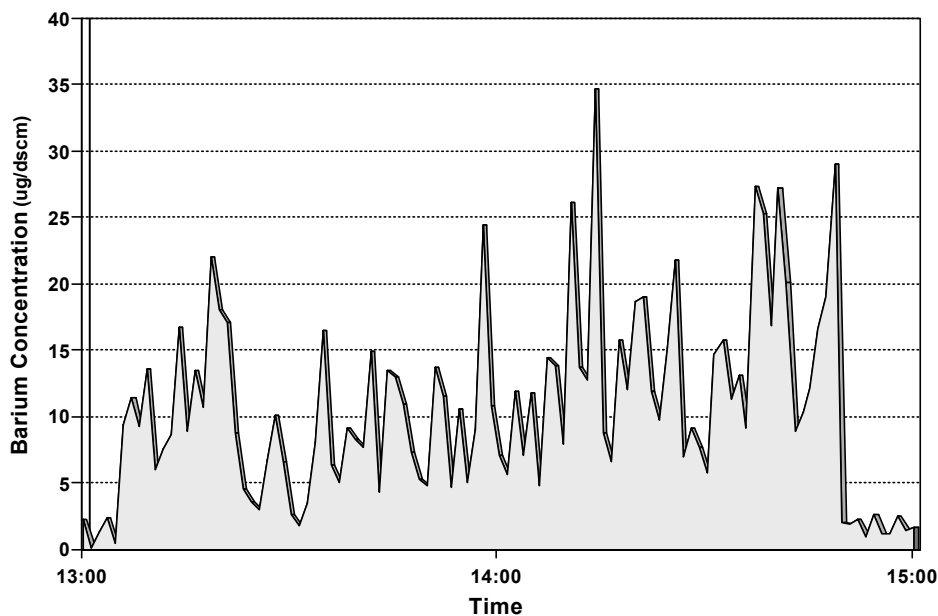


Figure 6. Barium emissions resulting from munitions deactivation

Metal Emissions Resulting from Artificial Introduction of Metal Aerosols

In order to evaluate the performance of the TraceAIR multimetals CEM over a wider range of metal elements than that represented by emissions associated with munitions items alone, it was necessary to introduce into the furnace exhaust gas matrix, a stream of dry, metal-containing aerosols. Using a proprietary apparatus, multi-element aerosols of known composition and approximate concentration were introduced into the furnace exhaust at a point downstream from pollution control equipment. These aerosols were introduced at a constant rate to support comparative measurements involving both the CEM and reference test method. Because the mass rate of aerosol introduction, and exhaust gas flow rate were known to a reasonable degree of certainty, it was possible to predict the approximate target concentrations of the various metals. Actual confirmation of these concentrations can be obtained only from the results of the

reference test methods. However, for the purpose of demonstration, it is reasonable to compare the CEM-detected metal concentrations with these “target” concentrations. Figures 7-9 depict the emissions of nickel (Ni), manganese (Mn), and cobalt (Co), introduced as dry aerosols, in the manner described above. Non-constant exhaust gas flow due to the actuation of a draft damping mechanism is responsible for the apparent variation in detected metal concentration.

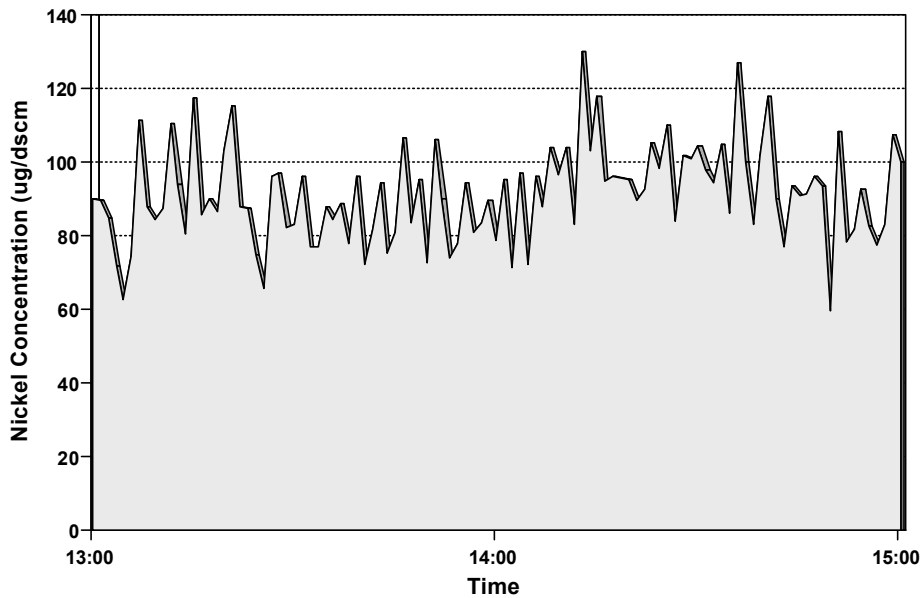


Figure 7. Nickel emissions resulting from artificial introduction of aerosols. Average nickel concentration: 91 $\mu\text{g}/\text{dscm}$; target concentration: 120 $\mu\text{g}/\text{dscm}$

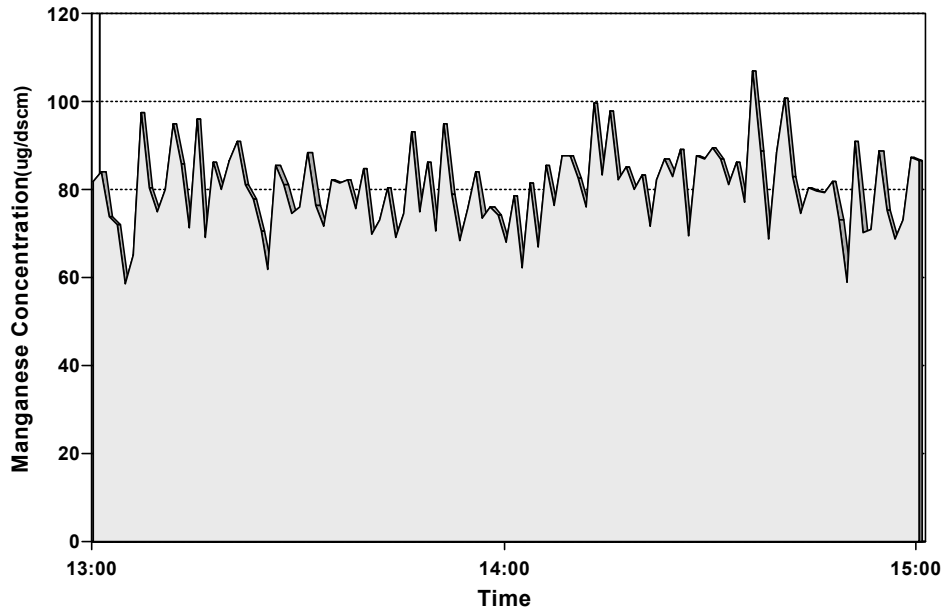


Figure 8. Manganese emissions resulting from artificial introduction of aerosols.
Average manganese concentration: 80 $\mu\text{g/dscm}$; target concentration: 90 $\mu\text{g/dscm}$

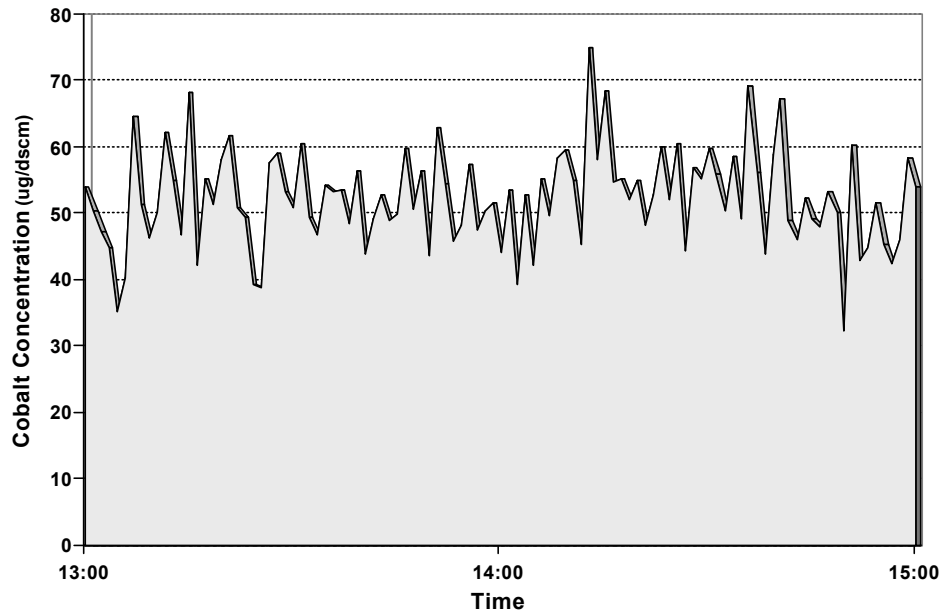


Figure 9. Cobalt emissions resulting from artificial introduction of aerosols.
Average cobalt concentration: 52 $\mu\text{g/dscm}$; target concentration: 60 $\mu\text{g/dscm}$

For each of the detected metals, an average concentration was calculated, based on the series of individual measurements made over the 2-hour period depicted in Figures 7-9. These averages are in satisfactory agreement with the predicted target concentrations of injected aerosols containing nickel, manganese, and cobalt, and therefore suggest that the shrouded probe-based sampling system has met expectations in terms of its performance, relative to the hardware and methodology used previously with less satisfactory results. A relative accuracy test audit (RATA), involving the results of 12 replicate reference method tests, conducted concurrently with CEM measurements, will confirm the enhanced performance of the TraceAIR multimetals CEM, and validate its ability to provide reasonably accurate and precise quantitation of stack gas metal concentrations.

Conclusions

As a result of the apparent improvements in the efficiency of sample collection and transport and the attendant benefits to measurement accuracy associated with the hardware modifications described above, the TraceAIR multimetals CEM promises to fulfill its potential as a legitimate compliance assurance tool. Further refinements and process improvements will be made as new applications and regulatory requirements demand.

References

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