Continuous Monitoring of Metals Emissions

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INTRODUCTION

Continuous monitoring of emissions can assure the public of the safe operation of combustion facilities. Because of this, continuous monitors for many materials that have not been previously subjected to continuous measurement are being developed. Trace metals are one such material. A novel concept for the continuously monitoring toxic metals emissions, in gaseous and particulate form, has been developed and is being tested at Midwest Research Institute (MRI). The concept is based on the use of the SpinCon® gas-liquid contactor with an inductively-coupled argon plasma emission spectrometer (ICAP) or an ion chromatograph. This combination of technologies is called SPICAP. The SpinCon® uses a high-velocity cyclonic gas-flow to transfer both soluble gases and particles from a contaminated gas stream to a concentrated liquid medium. The liquid medium can be transported to an appropriate analytical device on a continuous, semi-continuous or batch basis.

As described by French and Durham[1], the most common approaches used to continuously measure concentrations of multiple metals are based on the measurement of emissions spectra generated when stack gas samples are subjected to strong excitation sources. The SPICAP system may be operationally more complex than these competing systems due to its requirement for a liquid medium. However, it is capable of concentrating metals in the liquid stream yielding lower detection limits. In addition, the SPICAP is currently the only system that is capable of collecting samples that can be used to continuously measure hexavalent chromium (Cr^{+6}) emissions.

MRI's development program consists of three concurrent tasks. In the first, a computational model of the capture processes is being developed and refined. This model was used to predict the capabilities of the device and suggest new areas of development. In the second task, a series of controlled laboratory experiments were conducted to evaluate system operation and performance. The final task involves conducting field tests using prototype units.

EQUIPMENT

The CEM developed by MRI is based on the patented SpinCon® gas sampling system[2]. This device transfers contaminants from a gas and concentrates them in a liquid. A simplified schematic of the device is shown in Figure 1. Gas samples are drawn from a stack through a Teflon line at a controlled rate. The line can be continuously rinsed as in the standard Cr^{+6} method[3]. Gas samples can then be passed through a saturation tower equipped with an air-atomized spray nozzle to cool and saturate the gas. The saturation tower is only used when sampling gases that are not saturated with moisture and are above approximately 200°C.

Gas samples then flow into a transition chamber from which they are drawn through a slit in the wall of the SpinCon®. The slit is cut tangentially into the wall of a cylindrical collection chamber forcing the gases that enter to flow horizontally around the interior circumference of the chamber. After one revolution the gases exit up the center of the cylinder. Liquid is introduced through a small hole in the wall of the collector. The cyclonic air flow forces the liquid to form a thin film on the wall of the collector. When the film encounters the slit, it is atomized to form a jet of fine droplets. The droplets move with the entering air across a chord of the collector and collide with the wall. After the collision, the film is reformed. The air flow is induced by a pump downstream of the collector. Air and liquid

flows are controlled independently. Decreasing the liquid flow relative to the air flow allows the device to reach lower detection limits at the expense of longer response times.

Figure 2 illustrates the mechanisms that control the capture of material in the device. As the particle laden air enters the device, it encounters a cloud of slow-moving drops that have just been formed by atomization of the film. Particles are transferred from the gas stream to the liquid by inertial impaction with these drops. The drops rapidly accelerate to the speed of the air jet. Within the cloud of drops, very small particles, those with diameters less than about 0.1 μm, move to the droplets due to Brownian diffusion and are collected. When the drops collide with the wall of the collector, the gas and liquid are separated and the film is reformed. The gases then move around the inner wall of the collector in a thin layer near the wall. Particles move outward toward the wall due to the centrifugal forces. Any particles that reach the wall of the collector or the liquid film will be removed from the gas stream.

The collection of vapors occurs primarily in the cloud of droplets. Any soluble vapors diffuse to the droplets and are absorbed into the liquid. The mechanisms are enhanced by the large quantity of available liquid surface area in the droplet cloud. Once the liquid reforms the surface film, the available surface area decreases significantly and little additional removal of gases occurs.

MODELING

A computational model based on the mechanisms described above has been developed. All of the mechanisms except Brownian diffusion are accounted for. Table 1 summarizes major components of the model and the associated computational approaches. The model was used to predict the effect of several operational parameters on the predicted collection efficiency of the device. Two parameters found to exert a strong influence on the collection efficiency were particle size and slit coverage.

Figure 3 illustrates the predicted capture of particles and gases at the baseline conditions summarized in Table 2. The zone where particles collide with stationary droplets captures 67 percent of the particles initially in the gas stream. Centrifugal forces resulted in the capture of an additional 27 percent of the particles initially present. The predicted overall particle collection efficiency for the baseline conditions was 94 percent on a mass basis. Significant collection of soluble vapors is predicted to occur only in the cloud of droplets. Baseline vapor collection is predicted to be 40 percent by mass.

Figure 4 illustrates the impact of particle diameter on the predicted collection efficiency. The calculated efficiency was close to 100 percent for particles greater than 3 μm in diameter and decreased rapidly for smaller particles. The collection of particles less than 0.1 μm in diameter is the device will probably be much greater than predicted due to the influence of Brownian diffusion.

The fraction of the slit covered by the liquid film was thought to be an important operating parameter. When the film completely covers the slit, 90 percent of the particulate mass is captured by impaction in the spray and another 7 percent is captured in the centrifugal zone. When the fraction of the slit covered is decreased, the fraction of the material captured in the spray decreases proportionally. However, the relative quantity captured in the centrifugal zone increases. The overall capture efficiency decreases only slightly as the fraction of the slit covered by liquid decreases. Because most gas capture occurs in the droplet cloud, the capture of vapors is a strong function of slit coverage.

LABORATORY TESTING

The system's ability to collect hexavalent chromium has been tested in the laboratory[4]. Hexavalent chromium was selected as the target metal for these tests for three reasons. First compounds containing hexavalent chromium are often much more volatile than compounds containing the more common trivalent chromium. In combustion systems, compounds containing hexavalent chromium will vaporize in the high temperature regions and then condense as the gases cool. These processes result in the formation of particles typically about 0.2 μm in diameter. Particles in this size range are the most difficult to capture in most collection devices. Second, none of the multiple metals CEMs under development are capable of determining chromium speciation. Third, hexavalent chromium is a potent carcinogen and of significant environmental concern.

A DeVilbiss nebulizer was used to generate an aerosol consisting of particles composed of CrO_3. The aerosol was sampled using the SpinCon®, the standard EPA method for hexavalent chromium[3] and an inertial impactor. The collected material was analyzed for Cr^{+6} using ion chromatography. The results of these tests are summarized in Figure 5. The concentrations of Cr^{+6} found in the SpinCon® solutions were within 11 percent of those in the solutions produced by the standard method.

FIELD TESTS

Two series of field tests have been conducted using prototype sampling units. It both test series, samples of the collection liquid were obtained and shipped to an off-site laboratory for analysis. The tests were conducted at a hazardous waste incinerator and a mixed waste incinerator.

Hazardous Waste Incinerator

In these tests, the SpinCon® sampler was used concurrent with a standard EPA hexavalent chromium sampling train at a hazardous waste incinerator. Figure 6 summarizes the results of the tests. Much variation was observed because the emitted concentrations were close to the detection limits of the testing methods used. The detection limit of the SpinCon® system can be lowered by retaining the liquid in the collector for a longer period. However, that approach was not used in the field tests. No particle size analysis was performed. Due to the mechanism described previously, the particles containing the hexavalent chromium probably ranged in size between 0.2 μm and 1 μm.

The relative accuracy of MRI's approach was assessed using draft EPA performance specifications for multi-metals continuous emissions monitoring systems[5]. The documents specify two criteria for assessing the relative accuracy of an experimental CEM. The relative accuracy of the experimental method must be:

- Within ±20 percent of the mean value of the EPA reference method
- Within ±10 percent of the applicable standard.

The relative accuracy obtained using the SpinCon-based approach varied from that for the EPA reference method by 27 percent. However, the relative accuracy was calculated to be 7.1 percent of the applicable standard. Thus, the system conformed to the second criteria.

Mixed Waste Incinerator

The second series of tests were conducted at the U.S. Department of Energy Oak Ridge Reservation, located near Oak Ridge, Tennessee. A mixed waste incinerator designed and permitted for thermal destruction of radioactively contaminated polychlorinated biphenyl (PCB) and other hazardous compounds. Emissions were measured using the SpinCon-based system and EPA Method 29 simultaneously. Thirteen metals were targeted—antimony, arsenic, barium, beryllium, cadmium, chromium, lead, silver, manganese, cobalt, nickel, selenium, and uranium.

Figure 7 summarizes the results of the testing. The data show that the SpinCon-based unit generally indicated lower metals concentration than Method 29. However, the concentrations of all but four metals were below 10 µg/dscm. As these low levels, small variations in measured concentrations result in large relative errors.

For the four metals present at concentrations above 10 µg/dscm (Ba, Pb, Sb, and U), the EPA Method 29 results are higher that the CEMs results by a factor ranging from 1.1 up to 3.0. This difference may be caused by carryover of liquid from the sampler which removes some of the metal analytes. More recent improvements in the collector's level control system have reduced this problem.

CONCLUSIONS

The development of the SpinCon® sampler is an ongoing project at MRI. Testing and modeling work indicate that the CEMs is promising and has several unique capabilities. These include:

- Efficient collection of fine particles and soluble vapors.
- High gas sampling rate
- Low liquid volume and flow rate
- Adjustable concentration ratio (i.e., the ratio of the concentration of the component captured in the liquid to the concentration of the component in the gas being sampled).
- Capable of detecting hexavalent chromium

However, additional development is needed before the device can be commercially available.

REFERENCES

1. French, N. B., and Durham, M. "A Status Report in Multi-Metal CEM Technologies," *1996 International Conference in Incineration and Thermal Treatment Technologies*, Savannah, GA, 1996.
2. Cage, B.R. and Drinkwine, A.D. (to Midwest Research Institute) U.S. Patent No. 5,011,517, 1991.
3. "Determination of Hexavalent Chromium Emissions from Stationary Sources (Method 29);" *Methods Manual for Compliance with BIF Regulations Burning Hazardous Waste in Boilers and Industrial Furnaces*; PB 91-12006; U.S. Environmental Protection Agency, 1990.

4. Gormnan, P.G. and Hinshaw, G.D. "Progress in Development of a Continuous Monitor for Metals and for Cr+6," in *Proceedings of the 1995 AWMA Annual Meeting*, Air and Waste Management Association, 1995.
5. "Draft Performance Specifications for Multi-Metals Continuous Emission Monitoring System," U.S. Environmental Protection Agency, September, 1994.
6. Lefebvre, A.H., "Twin-Fluid Atomization: Factors Influencing Mean Drop Size," in *ICLASS-91*, Gaithersburg, MD, 1991.
7. Wark, K., and Warner, C.F., *Air Pollution: Its Origin and Control*, Harper and Row, New York, 1981.
8. Geankoplis, C.J. *Mass Transport Phenomena,* Ohio State Bookstores, Columbus, OH, 1972.

Table 1. Modeling approaches used to investigate behavior of the SpinCon®.

Process	Approach
Atomization	Twin fluid atomizer (after Lefebvre[5])
Particle-Droplet Inertial Impaction	Modification of venturi scrubber model (after Wark and Warner[7])
Capture due to Centrifugal Forces	Force balance (similar to cyclone analysis)
Vapor Absorption in Film	Diffusion limited rate. Turbulent boundary layer (after Geankoplis[8])
Vapor Absorption in Cloud	Diffusion limited rate. Droplets and vapor have same velocity (after Geankoplis[8])

Table 2. Baseline conditions used in the model.

Parameter	Value	Units
Liquid Properties		
Surface Tension	72.12	dyne/cm
Density	0.9965	g/cm3
Viscosity	0.8532	centipoise
Heat of Vaporization	2.26×10^{6}	J/kg
Average Molecular Weight	18	g/mol
Solids Properties		
Density	2.28	g/cm3
Particle Loading in Gas	100	µg/m3
Mean Particle Diameter	2	µm
Standard Deviation of Size Distribution	1	µm
Gas Properties		
Density	1.179×10^{-3}	g/cm3
Viscosity	1.97×10^{-5}	centipoise
Vapor Contaminant Concentration	100	µg/m3
Diffusivity of Vapor in Bulk Gas	0.288	cm2/s

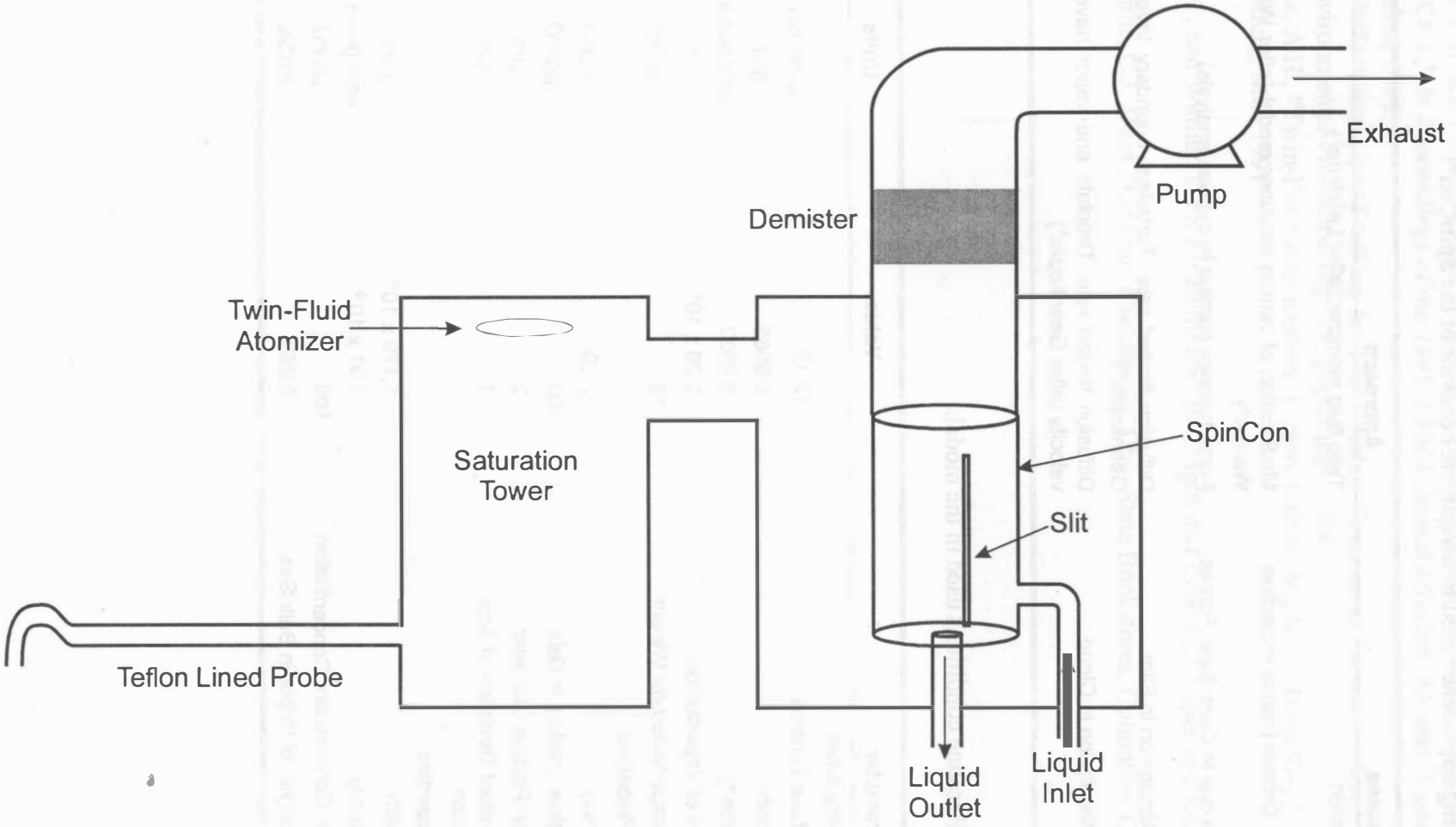

Figure 1. Schematic diagram of the SPICAP system.

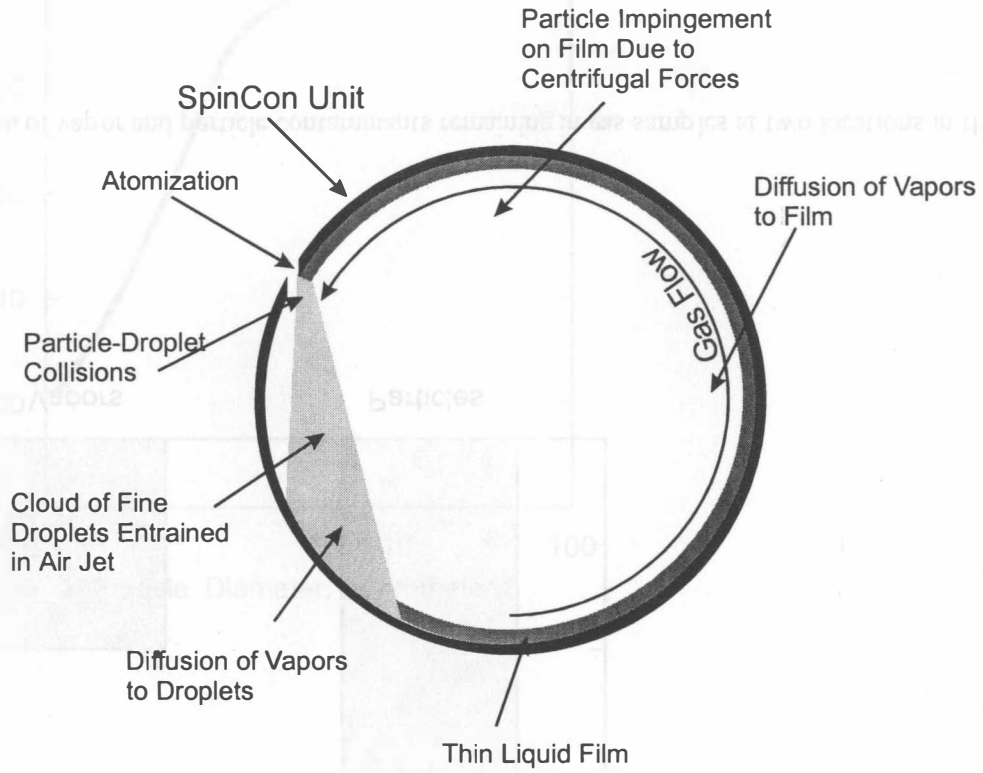

Figure 2. Mechanisms that control the collection of metals in a SpinCon collector.

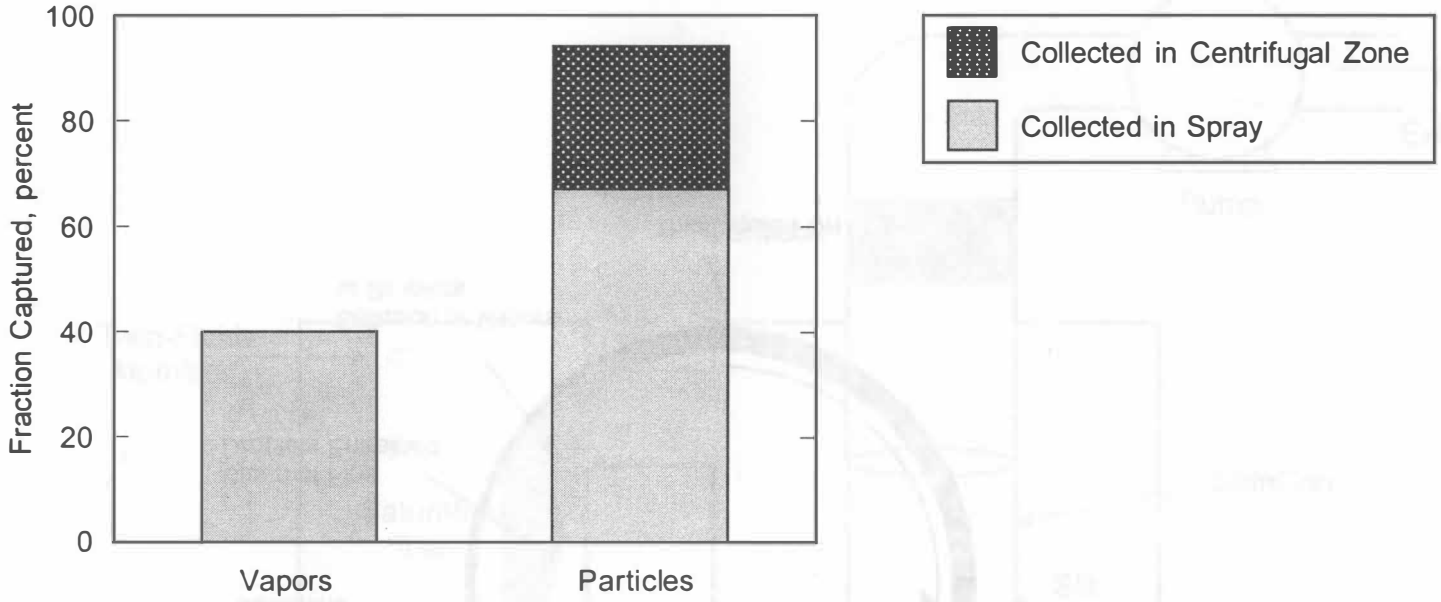

Figure 3. The predicted fraction of vapor and particle contaminants remaining in gas samples at two locations in the SpinCon collector.

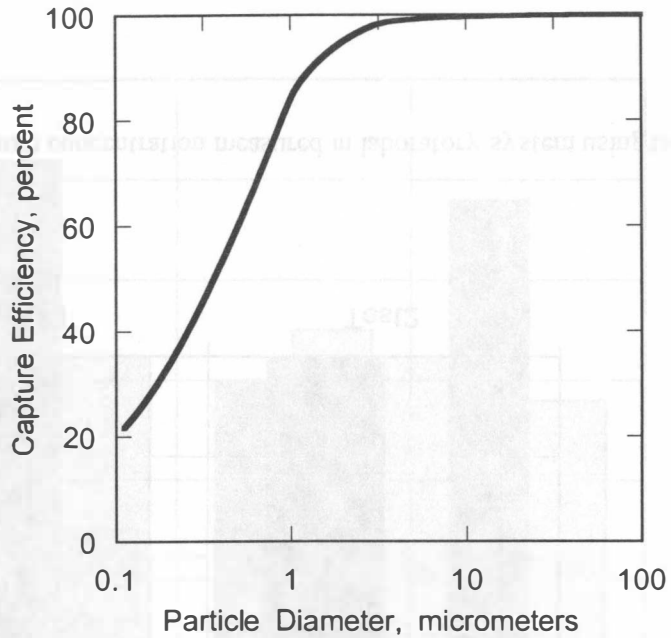

Figure 4. The predicted impact of particle size on capture efficiency.

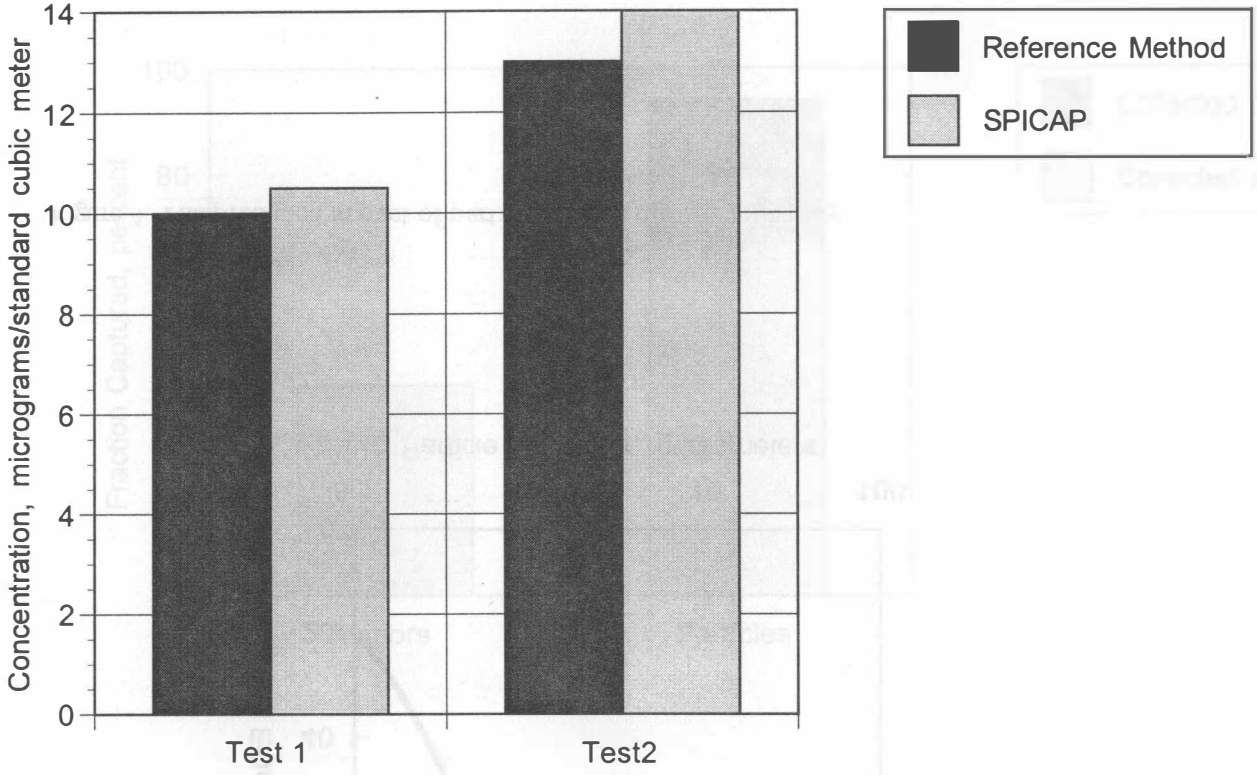

Figure 5. Hexavalent chromium concentration measured in laboratory system using the SPICAP and the EPA reference method.

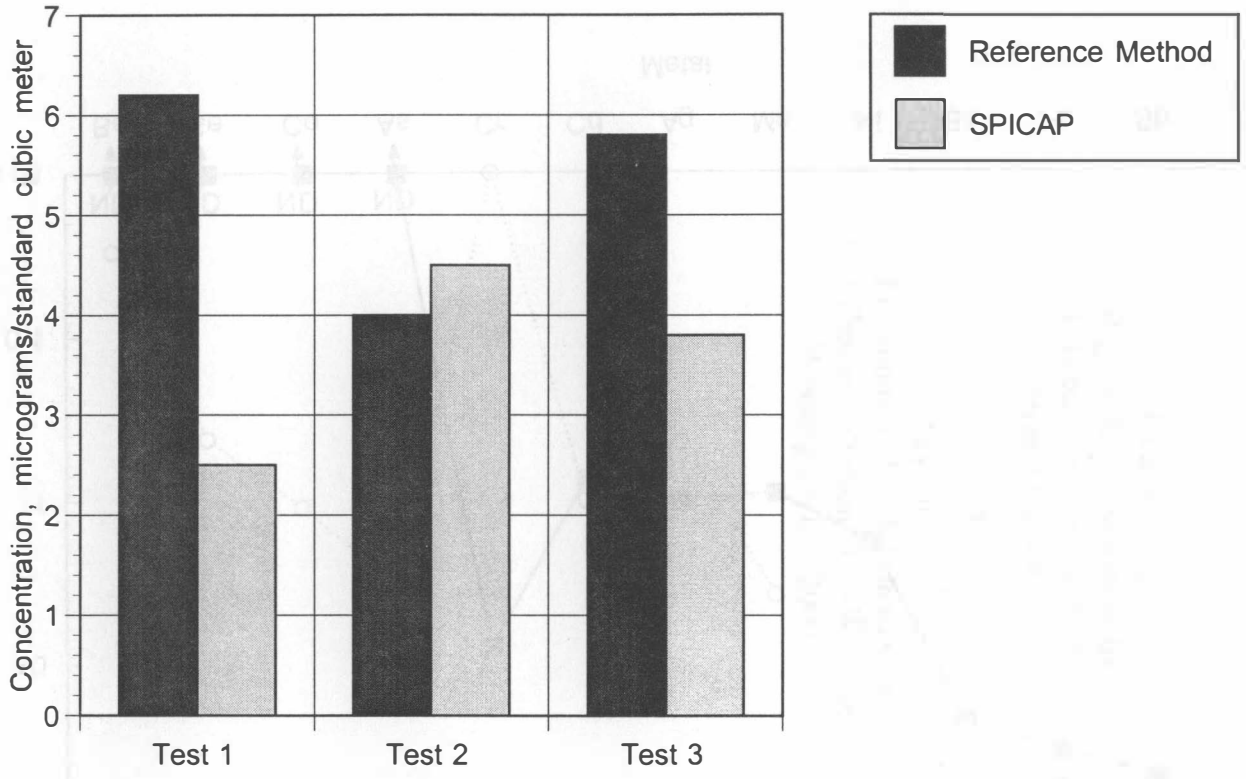

Figure 6. Hexavalent chromium concentration measured in incinerator exhaust gas using the SPICAP and the EPA reference method.

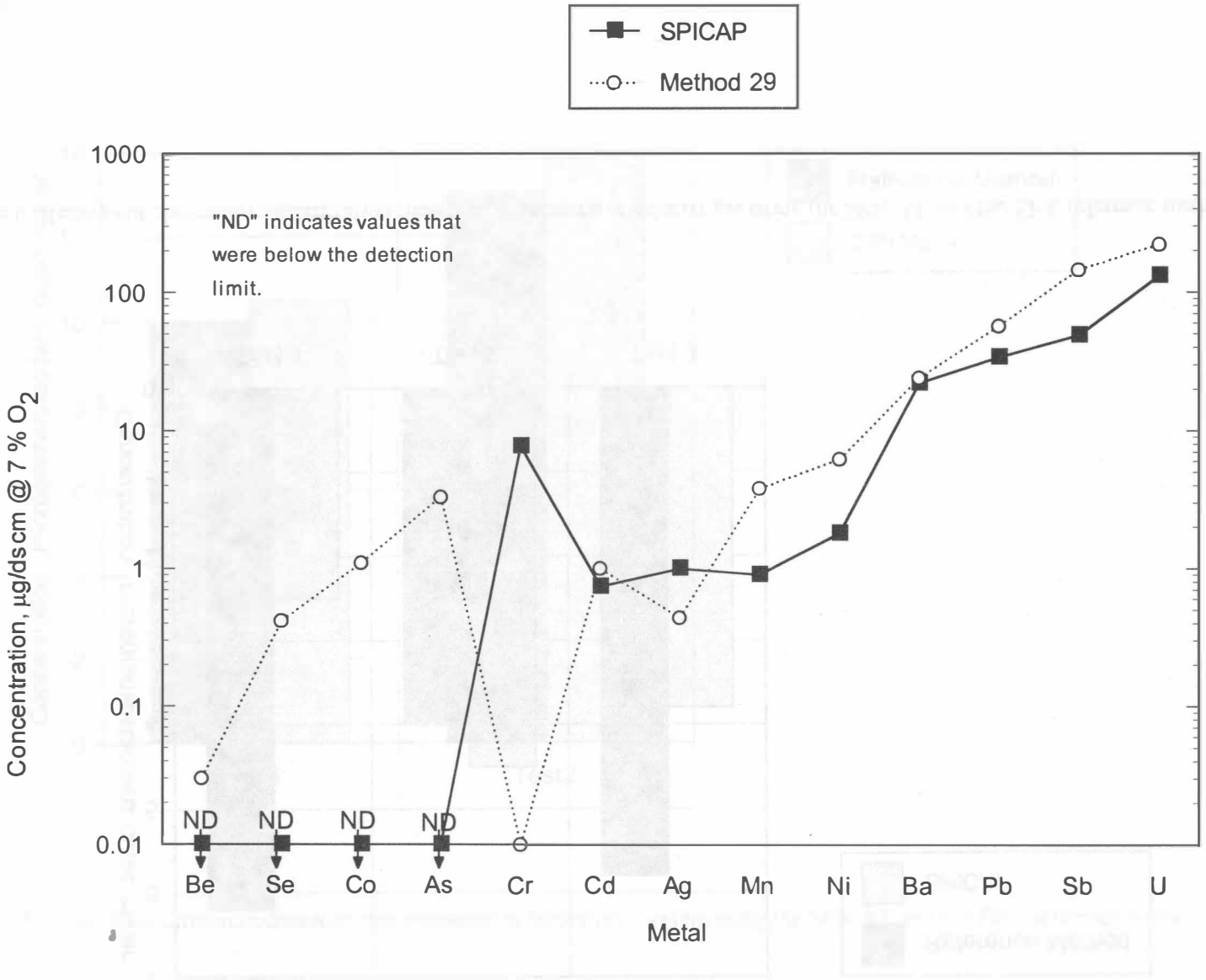

Figure 7. Results of sampling the exhaust gas of a mixed waste incinerator using SPICAP and the EPA reference method.