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Comparison of Atomization Sources for a Field-Deployable Laser Optogalvanic Spectrometry System

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A field-deployable laser optogalvanic spectrometry (LOGS) system has been developed to measure the concentration of metal species present in the near-atmospheric pressure off-gases of mixed-waste thermal-treatment systems, where metal species occur primarily as airborne metal oxide and/or metallic particles rather than as free, single atoms. Atomization is required to simplify the analyte and facilitate the detection of low concentrations. A comparative study of different LOGS atomization sources (electric glow discharge, radio frequency discharge, flames) was performed with respect to the feasibility of deploying each source. The advantages and disadvantages of the various atomization sources are discussed in terms of real-time monitoring, ease of operation, and ruggedness for field deployment. Although the various atomization sources permit a wide variety of laboratory-based LOGS applications, it is concluded that a flame-based atomization source is best suited for a field-deployable LOGS system to monitor airborne metal species in near-atmospheric pressure off-gas systems. Flame-based LOGS systems are usually referred to as laser-enhanced ionization spectrometry systems.

Nomenclature

A = atom
A^* = electronically excited atom
C_L = limit of detection concentration
D_{10} = drop diameter below which 10% of cumulative aerosol volume is found
D_{50} = drop diameter below which 50% of cumulative aerosol volume is found
D_{90} = drop diameter below which 90% of cumulative aerosol volume is found
e^- = electron
h = Planck's constant, 6.626×10^{-34} J · s
S = sensitivity, slope of calibration curve at lower concentrations
ν = frequency of photon, s^{-1}
σ_B = standard deviation of background signal

Introduction

LASER optogalvanic spectrometry (LOGS) has long been recognized as a well-developed spectroscopic technique for various applications, such as laser wavelength calibration,[1] spectral analysis of atoms and molecules,[2] and isotopic shift measurements of complex atoms,[3] and as an extremely sensitive detection tool.[4,5] LOGS has been used for direct detection of metal species at ultralow concentrations in flames and electric discharges. LOGS has been developed as an ultrasensitive diagnostic tool for on-line, real-time measurements of the concentration of volatile, toxic trace metals, radionuclides, and other gas-phase pollutants in the near-atmospheric-pressure off-gases of mixed-waste thermal-treatment systems, where metal species exist primarily as airborne metal oxide and/or metallic particles rather than as free, single atoms. The treatment of mixed low-level hazardous wastes places a great demand on the off-gas handling system. For new thermal waste treatment systems to be accepted by the public, the technology must demonstrate continuous compliance with environmental regulations, which is only feasible by utilizing real-time monitors. Real-time monitoring of airborne contaminants plays a vital role in the protection of personnel and in safeguarding the environment.

The optogalvanic effect is the change of the electrical impedance of a plasma when the incident laser radiation is tuned to an absorption of a species present in the plasma. A LOGS signal can be produced by laser-assisted electron impact ionization

$$A + h\nu \rightarrow A^* \tag{1a}$$

$$A^* + e^- \rightarrow A^+ + 2e^- \tag{1b}$$

where A may or may not be electronically excited; or by direct photoionization

$$A + h\nu_1 + h\nu_2 \rightarrow A^+ + e^- \tag{2}$$

where, in the most general case, $\nu_1 \neq \nu_2$, and more than two photons can be involved. Gas-phase species are required for LOGS; they can be produced by a variety of atomization sources, such as flames, planar glow discharges, hollow cathode discharges, radio frequency (rf) discharges, and microwave discharges. In the case of flames or dc discharges, the change of impedance can be monitored as a transient voltage change if a high-voltage electrode relative to ground is inserted into the plasma. [In flames, LOGS is more commonly referred

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to as laser-enhanced ionization (LEI) spectrometry.] In an rf discharge, the LOGS signal is extracted by a pickup coil wound around the discharge cell so that the discharge plays the part of a transmitting antenna and the coil plays that of a receiving antenna. Regardless of the atomization sources, the LOGS signal can be either positive or negative, depending on the transition probed and the role of that transition in maintaining the plasma.

Because the amplitude of the LOGS signal can be related to concentration, LOGS has the capability of monitoring, in real-time, the concentration of species of interest. LOGS alleviates problems associated with monitoring weak absorption or weak fluorescence in the presence of a strong optical background signal. In LOGS, the laser provides selectivity by only exciting the species of interest, and electrical detection provides enhanced sensitivity. Because its detection is electrical rather than optical, LOGS has the inherent capability of detecting species at lower concentrations than is possible with optical detection, because the collection of charges can be more efficient than the collection of photons.

Most of the metal species in the off-gases are expected to exist as airborne metal oxide and/or metallic particles; consequently, atomization is required to simplify the analyte and facilitate detection of low concentrations. In this paper, the results of our comparative study of different LOGS atomization sources (electric discharge, rf discharge, and flames) for use in a field-deployable LOGS system are reported. The advantages and disadvantages of the various atomization sources are discussed in terms of real-time monitoring, ease of operation, and ruggedness for field deployment.

Apparatus

The experimental apparatus is shown in Fig. 1. A LOGS experiment is performed using a tunable laser to detect different metal species (such as As, Cd, Cr, Hg, Ni, Pb, Sb, and U). The laser is tuned to a selected absorption of the species of interest. The dye laser beam [after frequency doubling and wavelength separation (by a four-prism harmonic separator), if necessary] is directed into the atomization source. Sample solutions of metal species for optogalvanic signal calibration are prepared by volumetric dilution of 1000 μg/mL (alias parts-per-million, ppm) standard solutions in an appropriate acid diluent using class A volumetric glassware, which has a measurement uncertainty of ±0.2% at 20°C; the standard solutions are metal salts dissolved in 2% acid solutions. Desolvated metal oxide particle aerosols are generated using an ultrasonic nebulizer (USN) and are then transported to the atomization source via a carrier gas. The LOGS signal generated in the atomization source is amplified and displayed on an oscilloscope for visual monitoring, and transferred to a gated integrator and data acquisition system for recording.

In the off-gases of mixed waste thermal treatment systems, metal species are expected to exist primarily as airborne metal oxide and/or metallic particles rather than as free atoms. An ultrasonic nebulizer is used because the desolvated metal oxide particle aerosol produced is expected to be a better approximation to airborne particles in the off-gases than pneumatically nebulized solution droplets. The ratio of metal/metal oxide within the USN particles is expected to be a function of the element, carrier gas (air in our case, but helium or argon for most USN users), carrier gas flow rate, anion, and the acid used. To our knowledge, there are no studies of the metal/metal oxide ratios of the particles produced by the USN using air as the carrier gas, but the metal oxide is generally expected to predominate over the metal. The literature[6] shows that the distribution of particles generated by USNs under our experimental conditions (0.85 l/min airflow rate and 2.2 ml/min solution flow rate) typically have Sauter mean diameters of 3–4.5 μm, where the Sauter mean diameter is defined as the volume-to-surface area ratio for the entire particle population. This mean particle size is larger than expected (~1 μm) after the particle filter of typical industrial off-gas systems, but comparable to or smaller than that expected before the particle filter; the mean particle size before the particle filter is dependent on facility parameters. The width of the USN particle distribution is described in terms of span[6]

$$\text{span} = (D_{90} - D_{10})/D_{50} \tag{3}$$

For USNs, the values[6] of the span range from 0.5 to 1.4. The width of the USN particle distribution is smaller than that from pneumatic nebulizers and glass frit nebulizers.[6] We did not determine the mean particle diameter for our apparatus, but expect this to be comparable to the literature[6] values and to particles found before the off-gas particle filter in industrial-scale, thermal-treatment systems. Moreover, it should be pointed out that in thermal treatment systems, the exact composition and the metallic/metal oxide ratio are expected to be functions of temperature, element, air pressure, airflow rate (as it relates to dwell time), the presence of other chemical species, and facility parameters; all of these factors are expected to change, especially for the treatment of mixed hazardous waste where the waste treated at one instant of time may be completely different than what is in the next batch. In this situation, no one chemical composition or metallic/metal oxide ratio can be taken as being universally descriptive of the particles. However, if the LOGS atomization source is efficient, the particles (whether metallic and/or metal oxide) will be atomized and

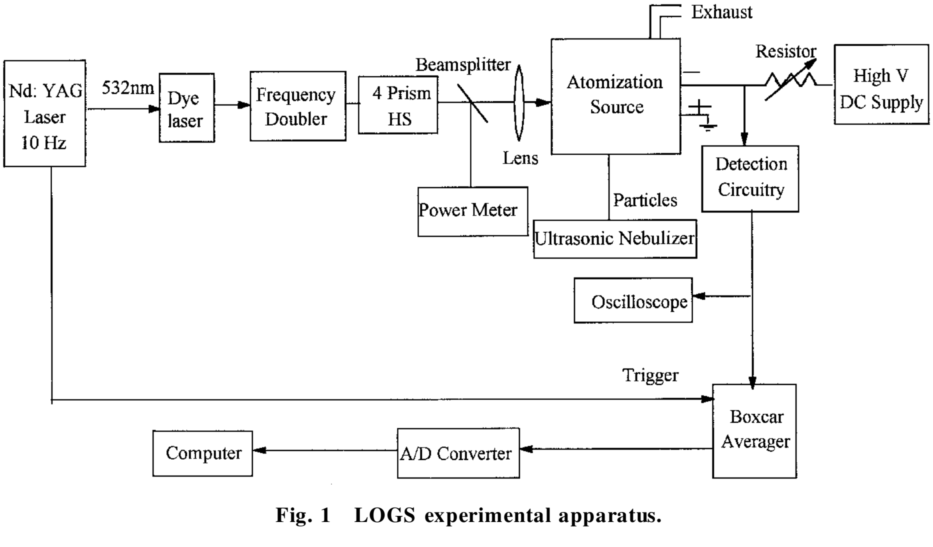

Fig. 1 LOGS experimental apparatus.

the analysis simplified, and it may not be necessary to take into account the exact composition and the exact metallic/ metal oxide ratio.

Different atomization sources require different experimental apparatus for generating a plasma. The hollow cathode-based atomization source (Fig. 2) consists of a custom-made discharge cell containing the hollow cathode and anode. The cathode is a brass hollow cylinder with an i.d. of 4.5 mm and 20 mm in length; the brass hollow anode has an i.d. of 5.5 mm and a length of 5 mm. The electrodes are placed concentrically about 5 mm apart inside the discharge cell. A 10-Hz Nd:YAG laser is used to pump a tunable dye laser. The dye laser beam is directed coaxially into the hollow cathode cylinder. The cell is maintained at low pressure, varying from 0.1 to 5 torr as monitored by means of a 10-torr full-scale Baratron-type pressure gauge. Air is used as the carrier gas. The discharge cell is operated at constant current. The dc current source is typically operated in the constant current mode at +400V with respect to ground. Operating currents up to 20 mA are used. The load resistance *R* is varied to obtain the same current at all relevant power supply voltages. The current source is connected to the discharge cathode and anode through a vacuum feedthrough. The metal oxide aerosols are fed into the discharge cell through an input port and continuously exhausted from the diagonal output port (Fig. 2).

The rf discharge-based atomization source (Fig. 3) consists of a discharge tube 8 mm in diameter with copper electrodes (5 cm apart) wound around the exterior of the tube.[7,8] A resonantly tuned pickup coil, also wound around the discharge cell and situated 1 cm below the lower electrode, is used to extract the desired LOGS signal. Sufficient rf voltage is applied to sustain a stable, low-noise discharge at low pressure of carrier gas (air). A flashlamp-pumped dye laser is used transversely for plasma excitation. This excitation geometry provides better linearity of the LOGS signal with respect to laser intensity; moreover, this geometry is often more sensitive and permits the probing of different plasma regions.[7,8] The pulse width of the laser (1 μs) extends over several rf oscillations, eliminating the need for precise synchronization between the laser pulse and the rf power supply.

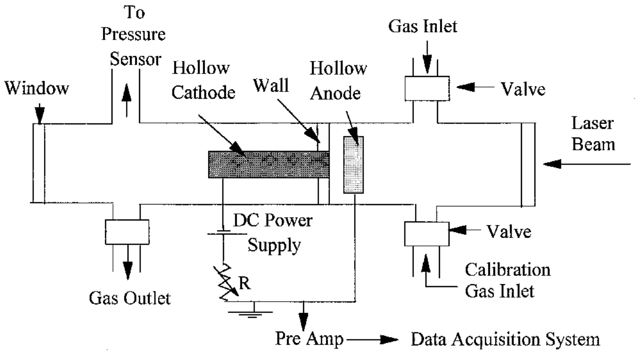

Fig. 2 Hollow cathode discharge-based atomization source.

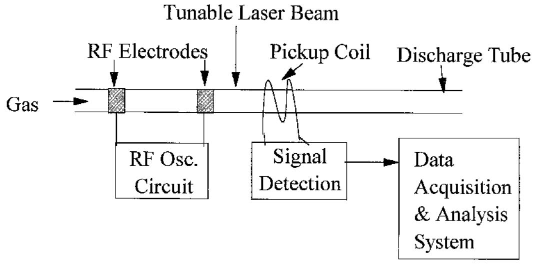

Fig. 3 Radio frequency discharge-based atomization source.

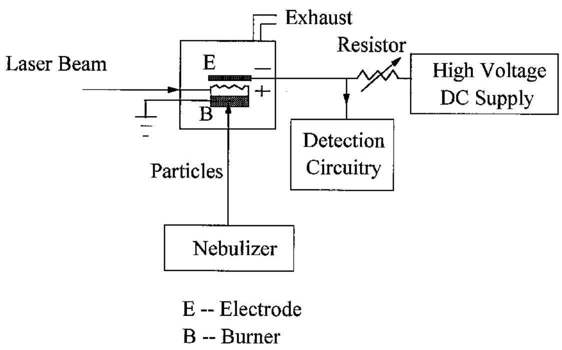

Fig. 4 Flame-based atomization source.

The flame-based atomization source (Fig. 4) consists of a premixed atomic absorption-type air/acetylene burner system with a 5-cm long, single slot. The burner's pneumatic nebulizer is not used for aspirating the solutions; rather, the sample aerosols produced by the ultrasonic nebulizer are fed directly to the burner system. A conventional atomic absorption burner has three inlets (one each for fuel, auxiliary fuel, and air). In our experiment, the auxiliary fuel inlet is used to introduce metal oxide aerosols into the burner. The burner assembly is enclosed in a cell so that toxic fumes can be exhausted. The flame is fed with commercial-grade acetylene and compressed ambient air in nearly stoichiometric proportions. A tungsten welding rod is used as the high-voltage electrode and is positioned 1.5 cm above the burner head to collect LOGS signal. The laser-beam orientation is the same as in the hollow cathode setup; it is incident on the flame parallel to the electrode and is in between the electrode and the burner. An XYZ translational stage is used to vary the distance between burner and electrode.

Results and Discussion

Because of the desire to avoid complications associated with combustible gases in flame systems, evaluations of electric discharge-based atomization sources were performed first. To our knowledge, there are no LOGS limits of detection (LODs) reported in the literature for metal species in planar glow discharges, hollow cathode discharges, or low-power rf discharges.

Planar Glow Electric Discharge-Based Atomization Source

Preliminary tests on a planar glow discharge atomization source proved unsatisfactory. Figure 5 schematically illustrates the different regions of a planar electric glow discharge and how the magnitude of the electric field *E* changes across the discharge. When exciting in the cathode fall region (regions 1–3 of Fig. 5), the magnitude of the LOGS signal is a very sensitive function of the distance between the laser beam and the cathode, because most of the voltage drop across the planar glow discharge occurs in the cathode fall region, which is typically only 2 mm thick.[9] Thus, the laser beam position must be maintained within 0.01 mm to avoid changing the LOGS sensitivity due to positional changes. While this positional alignment requirement is feasible in the laboratory, it is difficult to either achieve or maintain in the field. The positional

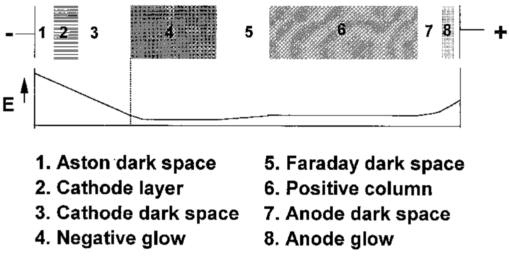

Fig. 5 Schematic (not to scale) of the regions of a planar electric glow discharge and the manner in which *E* changes across the discharge. The figure is adapted from von Engel.[8]

sensitivity of the LOGS signal in the cathode fall region of a planar glow discharge has the effect of increasing the measurement uncertainty and, hence, raising the LODs. Moreover, the thickness of the cathode fall region is inversely related to pressure[9]; thus, pressure fluctuations can also change the electric field at the excitation point and change the LOGS sensitivity.

In the negative glow region of a glow discharge, the electric field, on the other hand, is almost constant, and the positional sensitivity of the relatively narrow cathode fall region does not occur.[9] However, the LOGS signal obtained by excitation into the negative glow region is either very weak or nonobservable, because the cations that are produced tend to be collisionally neutralized before they can be detected at the cathode. Consequently, while LOGS in a planar glow discharge can be useful in a wide variety of laboratory applications, we conclude that a planar glow discharge atomization source is not convenient for field deployment.

Hollow Cathode-Based Atomization Source

A hollow cathode discharge atomization source is preferable to a planar glow discharge source for the following three reasons:

1) Electron density in a hollow cathode is much greater than in a planar glow discharge[9]; therefore, the probability of producing a LOGS signal by laser-assisted electron impact ionization [Eq. (1)] is increased.

2) The cathode fall region is thinner than that of a planar glow discharge, and so LOGS ions produced in the negative glow region can reach the electrode and be detected.

3) The thickness of the cathode fall region is not inversely proportional to pressure as it is in a planar glow discharge and, hence, the positional sensitivity for excitation is less in a hollow cathode.

To our knowledge, the only report in the literature of a limit of detection for LOGS detection of a metal species in a hollow cathode discharge is the report of Monts and Su,[10] using a sealed, static, commercial hollow cathode lamp. They estimate that their observed LOGS signal corresponds to detection of tens of nanograms of atomic silver. This suggests that, under proper conditions, LOGS LODs in a hollow cathode discharge can be very low.

To begin optimization of operating conditions (pressure, flow rate, voltage) in our custom-made hollow cathode discharge cell, a hollow cathode and anode setup was extracted from an old, commercial hollow cathode Pb lamp, in which the cathode is made of Pb. The LOGS hollow cathode discharge cell is filled with Ar as the carrier gas at various pressures ranging from 0.5 to 5 torr. It is easy to detect the Pb LOGS signal. We observed a maximum LOGS signal for the Pb transition at 283.3 nm when the Ar pressure was 1.5 torr. Because of oxidation of the electrodes that occurred when the electrodes were removed from the Ar-filled hollow cathode lamp, the LOGS signal deteriorated with time. After cleaning, the LOGS signal resuscitated, but could not be maintained.

Having found that the LOGS Pb signal could be detected in the hollow cathode cell, we switched to our custom-made hollow cathode electrodes. Argon was again used as the carrier gas. Initially, there were problems associated with cleaning of the cathode and anode, and also with sputtering. Extensive cleaning of the electrodes was done using methanol. The operation of commercial hollow cathode lamps as atomic line/calibration sources involves sputtering of the cathode metal. Because we wish 1) to monitor airborne metal species from the off-gases and avoid interferences caused by the material of which the apparatus is made, and 2) to prolong the electrode life (because the frequency with which electrodes are replaced must be minimized in a radioactive environment), we wish to operate the hollow cathode discharge so as to minimize sputtering from the electrode. Moreover, the sputtering also causes a ringing discharge. Sputtering was found to be reduced when the cell was maintained at low pressure for an extensive time after repeated evacuations and fillings with argon gas. After performing these steps, a stable discharge was maintained in our custom-made hollow cathode cell, and the LOGS signal for Ar was obtained at various pressures with flowing and static argon gas. It was noticed that the LOGS signal intensity was almost constant for periods of time exceeding half an hour.

When the system was running perfectly with flowing argon gas, lead particles were introduced into the hollow cathode cell from the ultrasonic nebulizer. After introducing the lead particles into the cell, it was found that: 1) a stable hollow cathode discharge is difficult to sustain for long periods of time, and 2) no Pb LOGS signal was detected at the 283.3-nm Pb transition. Attempts (also unsuccessful) were made to observe the Pb LOGS signal in a static cell that was filled with lead particle aerosols at various pressures. Our inability to observe a LOGS signal from lead particles is attributed to a combination of two factors. First, because electric discharges only operate at low pressures and the off-gas systems typically operate at near-atmospheric pressure, the airborne metal concentration must be reduced by a factor of ~200 to achieve discharge conditions of a few torr. Thus, because of the reduction of the effective sample size, relatively higher concentrations are required to observe a signal. Second, because electric glow discharges operate at 500–700 K, whereas flames and inductively coupled plasmas (ICPs) operate at or above ~2000 K, electric discharges do not atomize airborne particles as efficiently as do flames or ICP plasmas.

Because sodium and cadmium particles have low vaporization temperatures, we introduced airborne sodium and cadmium particles and looked for LOGS signals at 285.3 and 326.1 nm, respectively. No LOGS signals other than Ar LOGS signals were observed. Emission spectroscopy using a low-resolution photodiode array spectroscopy system was employed to see if there were any metallic emission lines in the discharge. We were able to observe Ar lines, but no metallic lines were detected, consistent with the hypothesis that atomization of metal particles in the hollow cathode discharge is not efficient. Therefore, it is concluded that although a hollow cathode discharge is an excellent atomization source for the study of gas-phase atoms and molecules in general, field deployment for detection of airborne toxic metal oxide/metallic particles is not feasible.

Low-Power rf Atomization Source

A low-power rf discharge atomization source has the advantage of involving no combustible gases and no internal electrodes and, hence, is free of issues associated with the corrosion/oxidation of electrodes. Attempts were made to detect atomic and molecular iodine in an rf discharge tube, using nitrogen and air as carrier gases under static and flowing conditions. The monitoring of radioactive iodine (^{129}I) vapors, which may be released from nuclear reactor wastes, is extremely important to a healthy environment. Molecular iodine is solid at room temperature, but sublimes to give a significant vapor pressure of I_2 (~178 mtorr at 22°C). For static cell investigations, a small amount of solid iodine is placed at the bottom of the discharge tube (~30 cm long). The discharge tube is then filled with nitrogen or air at selected pressures. The vapor pressure of iodine in the discharge tube was controlled by cooling the bottom end of the tube either in a circulating water bath chiller or a dry ice–acetone slurry. For investigations under flowing conditions, the iodine vapors are seeded into the nitrogen or air through a metering valve. The pressure difference at the inlet of the discharge tube, carrier gas pressure measured with and without seeding of the iodine vapor, gives the vapor pressure of iodine.

For rf powers below 0.5 and 1.5 W for flowing and static conditions, respectively, the rf discharge tends to oscillate (low-frequency relaxation oscillations). Above ~3 W, the plasma random noise starts to grow significantly. Figure 6

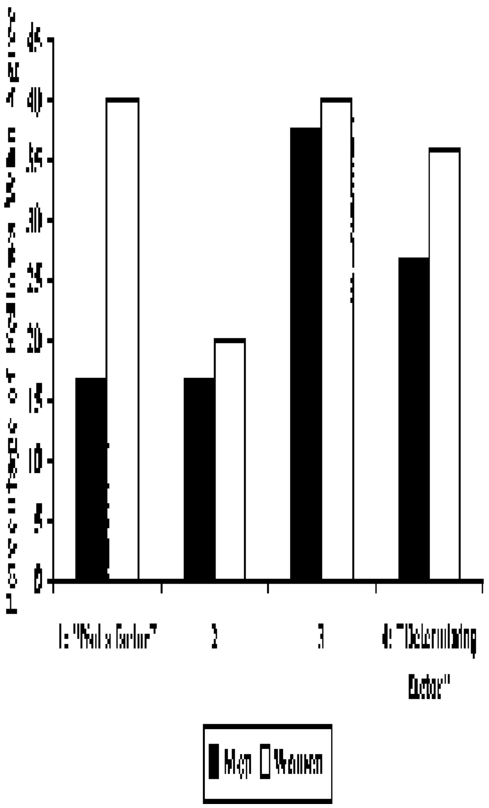

Fig. 6 RFLOGS signal for molecular I_2 and atomic I with different pressures of carrier gas. The pressure of the carrier gas (nitrogen) increases from the bottom panel to the top panel.

shows the radio frequency laser optogalvanic spectrometry (RFLOGS) signal for molecular iodine and atomic iodine at different nitrogen pressures. Note that it is possible to detect both atomic I and molecular I_2 simultaneously, and, by changing the pressure of carrier gas, to vary the relative amounts of atomic and molecular iodine. At lower carrier gas pressures, atomic iodine dominates, whereas at higher carrier gas pressures, molecular iodine dominates. Experiments were also repeated with flowing conditions for both air and nitrogen. It was found that the RFLOGS signal is larger in air than in nitrogen. We estimated the LODs from the ratio of the partial pressures of the detected species and the carrier gas. The LODs for iodine by RFLOGS are quite good. We have determined LODs for I_2 in air as low as a mole fraction of 0.2 ppm under static conditions and as low as 0.9 ppm under flowing conditions, and for I in nitrogen of 27 ppm under static conditions and 150 ppm under flowing conditions. Table 1 shows the experimental conditions for RFLOGS detection of molecular iodine in air under static conditions and the calculated LODs. The reported LOD values are the linearly extrapolated values that give a signal/noise ratio of 2 for a 5 mJ/pulse laser firing at 10 Hz rate at 16,980 cm^{-1} for molecular iodine and at 16,912 cm^{-1} for atomic iodine. These initial results are encouragingly close to the 0.0035 ppm airborne mole fraction LOD for atomic iodine in an oxidizing environment by inductively coupled plasma–atomic emission spectrometry (ICP–AES).[11] Further optimization of the RFLOGS operating conditions is expected to reduce the LODs for iodine to be comparable to or below that obtainable with ICP–AES.

Airborne sodium and cadmium particles were introduced into the discharge tube from the ultrasonic nebulizer, but the results were the same as for dc electric discharges. It is difficult to see the RFLOGS signal from airborne particles because of the following facts.

1) There is a very strong, broad RFLOGS background signal from a metastable state of molecular nitrogen. This background is significantly larger than the signal caused by Na, even when the laser is tuned to the strong *D*1 and *D*2 Na lines and we use undiluted 1000 μg/ml Na ICP standard solution in the ultrasonic nebulizer.

Table 1 RFLOGS LODs expressed as the mole fraction of molecular iodine in air[a]

Air pressure, mtorr	rf power, W	rf frequency, MHz	Laser energy, mJ	LOD, ppm
4800	0.5–1.0	32.070	1.63	0.2
1000	0.5	32.165	2.3	5.5
1000	1.0	32.165	2.3	42.0
1000	3.0	32.100	2.3	4.04
500	0.5	31.935	2.3	15.6
500	1.0	31.935	2.3	248

[a] Under static conditions where I_2 vapor pressure is 178 mtorr at 22°C and the excitation frequency is 16,980 cm^{-1}.

2) The RFLOGS signal deteriorates at higher rf power, because the background signal increases at a faster rate than does the RFLOGS signal of interest; thus, the signal-to-background ratio decreases with increasing rf power.

3) The RFLOGS detection sensitivity is also a function of the pressure, flow rate, and gas composition. Pressure and flow rate can be controlled, but one has no control on the change of gas composition in a real mixed-waste treatment system with a constantly changing feed composition.

4) RFLOGS operates at a few torr pressure; consequently, the off-gas sample must be diluted from near-atmospheric pressure, leading to higher LODs.

5) Although there are no internal electrodes to corrode or oxidize, the RFLOGS signal level can be significantly changed by depositions on the inside of the tube. These depositions are more frequently observed with air than with nitrogen or argon as the carrier gas. It was found during one experiment with iodine that the RFLOGS signal intensity decreased by a factor of 2 over a one-half-hour period because of deposition; by cleaning the tube, the former detection sensitivity level was regained. But frequent cleaning or replacement of the tube would not be desirable in a radioactive setting. Moreover, the effects caused by deposition on the inside of the tube raise questions about how frequently the system response must be calibrated and about the accuracy and reliability of the concentration determinations for on-line, real-time monitoring.

As described in the preceding text, RFLOGS is subject to two limiting factors that are generic to electric discharges. First, because the discharge only operates at low pressure, the near-atmospheric pressure off-gases must be diluted down to a few torr before testing. For example, a 1000-μg/ml Na solution (1000-ppm solution concentration) is diluted down to an airborne mole fraction of 480 ppm (at 20°C) before entering the RFLOGS excitation tube because of the limited efficiency of the ultrasonic nebulizer (~17.8% for our experimental conditions) and the volumetric increase associated with liquid-to-gaseous phase changes. For cases where the gas stream is at low pressure and a pressure reduction dilution of the sample is not required, RFLOGS may offer a viable alternative to flame-based LOGS. Second, because the excitation temperature of an electric discharge is typically only 500–700 K, the atomization efficiency of airborne metallic particles is less than that in higher temperature atomization sources.

It is concluded that although RFLOGS is a very valuable laboratory technique, it is not viable for continuous, on-line monitoring of metal species in the near-atmospheric pressure off-gases of a radioactive thermal treatment facility.

High-Power rf Discharge-Based Atomization Source

Before describing our efforts with flame-based atomization sources, note that there is an additional electric discharge atomization source that has been utilized for LOGS investigations: a high-power rf discharge such as that used in ICP--

AES systems. In contrast to planar glow discharges, hollow cathode discharges, and low-power rf discharges, there are published reports of measurements of LODs for optogalvanic detection in ICP plasmas. Several researchers have investigated optogalvanic detection in ICP plasmas, but, to our knowledge, the lowest detection limits are those of Ng et al.[12] They report LODs in an ICP plasma that are four to six orders of magnitude higher than those achievable by LOGS in a flame.[4,5] Moreover, the ICP LOGS LODs are higher than those obtained with an air ICP–AES system.[13] The reason for the high LODs in the ICP plasma is the high temperature of the plasma causes a significant amount of thermal ionization to occur; this makes it difficult to detect the LOGS-produced ions above the thermal ion background. Moreover, if the electrode is positioned low in the ICP plasma, great care is required to prevent arcing and rf interference. If an electrode is placed in the upper regions of the ICP plasma, the concentration of free atoms is significantly reduced and, hence, the LODs are increased. Because the LOGS LODs currently achievable in an ICP plasma are so much higher than LODs achievable by other means, ICP plasma was not further considered as an atomization source for a field-deployable LOGS system.

Flame-Based Atomization Sources

The feasibility of quantitative LOGS detection of metal species aspirated into flames has long been established.[4,5] LOGS in flames is generally referred to as laser enhanced ionization (LEI) spectrometry. To compare the limits of detection achieved with different fuels, we have pneumatically aspirated selected metal solutions into our burner system using methane (CH_4), MAPP (a stabilized methyl acetylene-propadiene mixture that is sometimes used in welding because it is safer than acetylene), and acetylene (C_2H_2) fuels. Air was used as the oxidant because the off-gas metal particles are entrained in it. The results are shown in Table 2.

The maximum flame temperatures of MAPP, methane, and acetylene in air are 1470, 1875, and 2125–2400°C, respectively. It is found that decreasing LOGS LODs correlate with increasing flame temperature (and, hence, with increasing atomization efficiency). This is consistent with the observation that the LODs for optogalvanic detection are relatively high in electric and rf discharges because the temperature is low and, hence, the atomization efficiency is also relatively low.

It should be noted that previous reports[4,5] of LOGS LODs refer to solutions aspirated into the flame by a pneumatic nebulizer that produces small droplets of solvated metal. As described in the preceding text, the metal species in off-gases are expected to consist primarily of dry, airborne particles rather than solvated, free atoms/molecules. Hence, an ultrasonic nebulizer better approximates the sample matrix found in off-gases than does a pneumatic nebulizer. Therefore, we have determined LOGS LODs for selected metals introduced into the burner system as airborne, desolvated metal oxide particles from an ultrasonic nebulizer. Table 3 compares LOGS LODs determined using an ultrasonic nebulizer with those determined by an air ICP–AES system[13] (a competing, on-line, real-time technology) and those currently sought by the U.S. Environmental Protection Agency (EPA) for continuous emission monitors (CEMs) of volatile toxic trace metals. LOD is defined as the concentration that produces a net line intensity equivalent to three times the standard deviation of the background signal obtained from a blank solution. This is evaluated from[14]

$$C_L = 3\sigma_B/S \tag{4}$$

It is seen that current LOGS LODs are comparable to or less than the air ICP–AES LODs and EPA's desired CEM LODs. Further optimization of the LOGS system can be expected to reduce the LODs by at least one order of magnitude and, in favorable cases, by up to three orders of magnitude. Thus, a flame-based LOGS system can detect metal species at and below environmentally mandated concentrations, and at and below concentrations that can be monitored by other on-line, real-time technologies.

Table 2 Comparison of pneumatically nebulized flame-based LOGS limits of detection (in mg/m^3) for different fuel mixtures[a]

Metal	Air/MAPP	Air/CH_4	Air/C_2H_2
Pb	0.4	0.15	0.008
U	4	1.8	0.004

[a] Where MAPP is a stabilized methyl acetylene-propadiene mixture.

Table 3 Comparison of limits of detection of LOGS, air ICP-AES, and current EPA CEM limits[a]

Metal	LOGS	Air ICP	EPA CEM
Ni	0.00078	0.0019	0.005
Pb	0.008	0.0047	0.050
Sb	0.012	0.270	0.005

[a] All values are in mg/m^3.

Conclusions

We have investigated a wide range of atomization sources (planar glow discharge, hollow cathode discharge, rf discharge, and flames) that have been employed in laboratory investigations utilizing the optogalvanic effect. We have found that the limits of detection for airborne metal oxide particles at near-atmospheric pressures are lower in flame-based atomization sources than in electric and rf discharge-based atomization sources. We attribute this to: 1) differences in atomization efficiency that can be correlated with temperature and 2) the dilution required to reduce the gas pressure from near-atmospheric to a few torr, the operating pressure of electric discharges. Thus, although the electric and rf discharge-based atomization sources have yielded and will continue to yield many important results in the laboratory, only flame-based atomization sources are viable for a field-deployable LOGS system for monitoring the concentration of metal species present as airborne particles in the near-atmospheric pressure off-gases of mixed-waste thermal-treatment systems.

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