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Instrumentation Evaluation and Development, Stormwater Effects and Control

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Abstract

Advanced laser fluorescence metal analyzers being developed and tested by the Department of Physics and the Department of Civil and Environmental Engineering at the University of Alabama at Birmingham (UAB), and with the General Physics Institute of the Russian Academy of Science, have several unique attributes compared to currently available instrumentation, including:

- Extremely low detection limits (<ng/L) and very small sample size requirements
- Confirmation of analysis with multi-line excitation
- Several metals can be simultaneously evaluated
- Extremely stable instrument and repeatable results

This paper describes a method used at UAB to evaluate the performance of field instrumentation, pointing out the current short-comings of available technologies for heavy metal analyses. A short description of the laser spectroscopic techniques being developed to satisfy some of these problems is also included.

Stormwater Effects and Analytical Method Requirements

The main purpose of treating stormwater is to reduce its adverse impacts on receiving water beneficial uses. Therefore, it is important in any urban stormwater runoff study to assess the detrimental effects that runoff is actually having on a receiving water. Urban receiving waters may have many beneficial use goals, including:

- stormwater conveyance (flood prevention)
- biological uses (warm water fishery, aquatic life, biological integrity, etc.)
- non-contact recreation (linear parks, aesthetics, boating, etc.)
- contact recreation (swimming)
- water supply

With full development in an urban watershed and with no stormwater controls, it is unlikely that any of these uses can be obtained. With less development and with the application of stormwater controls, some uses may be possible. It is important that unreasonable expectations not be placed on urban waters, as the cost to obtain these uses may be prohibitive. With full-scale development and lack of adequate stormwater controls, severely degraded streams will be common. However, stormwater conveyance and aesthetics should be the basic beneficial use goals for all urban waters. Aquatic life should also be a goal, but with the realization that the natural stream ecosystem will be severely modified with urbanization. Certain basic controls, installed at the time of development, plus protection of stream habitat, may enable partial use of some of these basic goals in urbanized watersheds. Careful planning and optimal utilization of stormwater controls are necessary to obtain these basic goals in most watersheds. Water contact recreation, consumptive fisheries, and water supplies are not appropriate goals for most urbanized watersheds. However, these higher uses may be possible in urban areas where the receiving waters are large and drain mostly undeveloped areas.

In general, monitoring of urban stormwater runoff has indicated that the biological beneficial uses of urban receiving waters are most likely affected by habitat destruction and long-term pollutant exposures (especially to macroinvertebrates via contaminated sediment), while documented effects associated from acute exposures of toxicants in the water column are rare (Field and Pitt 1990; Pitt 1995a and 1995b). Receiving water pollutant concentrations resulting from runoff events and typical laboratory bioassay test results have not indicated many significant short-term receiving water problems. However, it is important to not isolate individual runoff events and therefore not consider the accumulative adverse effects caused by frequent exposures of receiving water organisms to stormwater (Davies 1995; Herricks and Klaus 1996). Recent investigations have identified acute toxicity problems associated with moderate-term (about 10 to 20 day) exposures to adverse toxicant concentrations in urban receiving streams (Crunkilton, *et al*. 1997). Burton and Pitt (1998) have prepared a comprehensive book describing how to design and conduct an investigation to determine the specific causes of biological use degradation in receiving waters.

The most important metal contaminants in urban areas are usually copper, lead, and zinc, although other metals are also of interest (including aluminum, arsenic, cadmium, chromium, iron, mercury, and nickel). Table 1 shows typical urban area concentrations of these three metals. The filterable (dissolved) fractions for these metals is typically small for copper and lead (<20%) and higher for zinc (>50%) in most urban runoff waters. Even though the sediment concentrations for these metals may range from several 100 to several 1,000 mg/kg, the interstitial water concentrations of most interest may also be low. The required detection limit for these metals needs to be close to 1 µg/L (and even much lower for arsenic, cadmium, and mercury), especially if quantifying the filterable fractions of these contaminants. Available field methods for heavy metals typically have much higher detection limits, as noted in the following discussion.

Table. 1 Typical Heavy Metal Concentrations in Urban Waters, Compared to Nationwide Waters and Water Quality Criteria

All µg/L (range, and median)	Copper	Lead	Zinc
Nationwide U.S. waters	1 to 280 (15)	<1 to 890 (2)	<10 to 4,200 (20)
Urban rain water	Median of 10	Median of 50	Median of 50
Urban stormwater runoff	1 to 100 (50)	5 to 2,000 (100)	10 to 2,500 (200)
Urban snowmelt water	5 to 150 (50)	20 to 300 (100)	10 to 1,200 (300)
Combined sewer overflows	Median of 75	Median of 100	Median of 250
Household septage	<1 to 35 (6)	2 to 30 (8)	30 to 150 (50)
Well-treated sanitary sewage	6 to 50	3 to 350	4 to 350
Typical receiving water aquatic life criteria	5 (for very soft water) to 50 (for very hard water)	20 (for very soft water) to 200 (for very hard water)	100 (for very soft water) to 800 (for very hard water)

Evaluations of Field Methods for Monitoring Heavy Metals

There are many problems with current environmental sampling and analysis programs that can be met by conducting water quality evaluations in the field, especially if continuous, *in-situ* procedures are used. Foremost among these problems is the need to collect many samples in order to obtain the desired accuracy of the characteristics of interest. Other concerns involve inadvertent changes that may affect the sample characteristics between sample collection and analysis. The high costs of analyzing trace levels of organic and metallic toxicants using conventional laboratory procedures is also restrictive. Heavy metals are of great interest as they are possibly the most important toxic pollutants present in most receiving waters. Unfortunately, sensitive, simple, safe, and inexpensive methods for their determination are not available.

Relatively simple field test kits have been marketed in the U.S. for the past 30 years that can evaluate many parameters. However, few of these kits are suitable substitutes for conventional laboratory procedures. With care, good “screening” observations can be obtained from many of these kits. However, the sample collector, kit user, and data user must be aware of the limitations and hazards associated with many of these kits. The main concerns include:

- safety (safe and correctly labeled reagents and clear instructions, including disposal guidance)
- adequate sensitivity for required use of data
- problems with interferences
- ease of use and level of training needed
- cost

An important pollutant category that is not represented with any real-time field instrumentation is heavy metals. Samples require digestion in order to release all of the particulate-bound heavy metals for analysis. In addition, most metals are not amenable to real-time analyses. Current research at the University of Alabama at Birmingham (in conjunction with the General Physics Institute of the Russian Academy of Sciences and Alabama Laser) that is sponsored by the National Science Foundation has developed and demonstrated a laser-based instrument that may be capable of continuous heavy metal analyses in water. This instrument is extremely sensitive, as it is based on atomic fluorescence. The use of lasers enables the specific wavelengths most critical for analysis to be precisely used in the instrument. In addition, automated digestion of the samples may also be possible.

In a recent series of tests at UAB, 50 test kits were subjected to preliminary evaluations with half further subjected to more detailed tests. Safety hazards, cost, poor detection limits, matrix interferences, limited concentration ranges, poor response factors, and complexity of the test kits were all reasons for rejection. The "easiest" to conduct test and the "best" test in each category were then identified, after rejecting those kits that were much more expensive than alternatives in each category. The evaluation of the kits were based on five major tests:

1) subjective evaluations of the health and safety features (kit reagent contents, design features to minimize operator exposure to hazardous reagents, disposal problems and warnings),
2) performance using samples spiked with known pollutant additions in "clean" and "dirty" water,
3) comparisons with standard laboratory procedures using parallel analyses of typical samples,
4) repeatability and precision using replicate analyses, and
5) complexity of each method.

The first tests for each method used spiked samples. Two series of samples were prepared, one using ultra clean water prepared by ion exchange and reverse osmosis (RO), and another using a composite of parking lot runoff water. The clean water served as a control for identifying optimal test kit performance (assuming low ionic strength effects did not adversely affect the test). The parking lot runoff water was used to detect any significant matrix interferences. The spiked standards were evaluated by all methods for each parameter. Data were collected on "useful" range, capital costs, expendable costs, analysis time, health and safety considerations and "usability".

A plot of instrument response to spike concentration was made for each water type. This was used to estimate the range of linear response of the instrument. Ideally, the slope generated from these analyses (response factor) should be 1. A slope significantly different from 1 indicates a bias in the method. Also, the slope of the response for the clean water matrix should be the same as the slope of the response in the runoff water. The value of the standard error of the regression was used to estimate the detection limit of the method. Figure 1 is an example of a plot prepared for lead for two different test methods.

The residuals of the regressions were also examined to identify any evidence of bias. A plot of residual versus predicted spike concentration should produce a random band of points with an average value representing the concentration of the parameter of interest in the blank sample. Narrow error bands indicate a more precise method. A plot of residuals versus the order of analysis indicate if a bias is time dependent. For example, the calibration of a pH meter will drift over time. A plot of residuals versus the order of measurement will show a linear trend if the meter is not regularly re-calibrated. Figure 2 is an example residual plot for one of the lead test kits.

Two sets of field methods were identified for further study. The first set was defined by lowest detection limit with acceptable safety considerations. The second set was chosen on the basis of shortest analysis time with acceptable safety considerations and good ease of use. These selected methods were then further evaluated by parallel analysis for 25 runoff water samples. The test kit results were compared to the results obtained using standard laboratory procedures. This set of analyses were also analyzed by a regression technique to identify the correlation between field measurements and laboratory analyses. The precision of the selected methods were also evaluated by testing five replicates of a composite polluted water sample. The average, standard deviation and relative standard deviation (RSD, also known as the coefficient of variation) for the methods was determined for each test kit.

Most of the field test kits evaluated performed very well, with significant response factors and recoveries close to 1.0 (slopes of the regression lines when comparing known concentrations with test responses). In addition, the response factors were very close for spiked sample analyses in both clean and runoff sample water, indicating few matrix interference problems. The precision of the tests were also generally excellent, with almost all replicate analyses having COV values of less than 20% and many were much less than 10%. However, the detection limits of almost all of the analytical methods were much higher than reported by the manufactures.

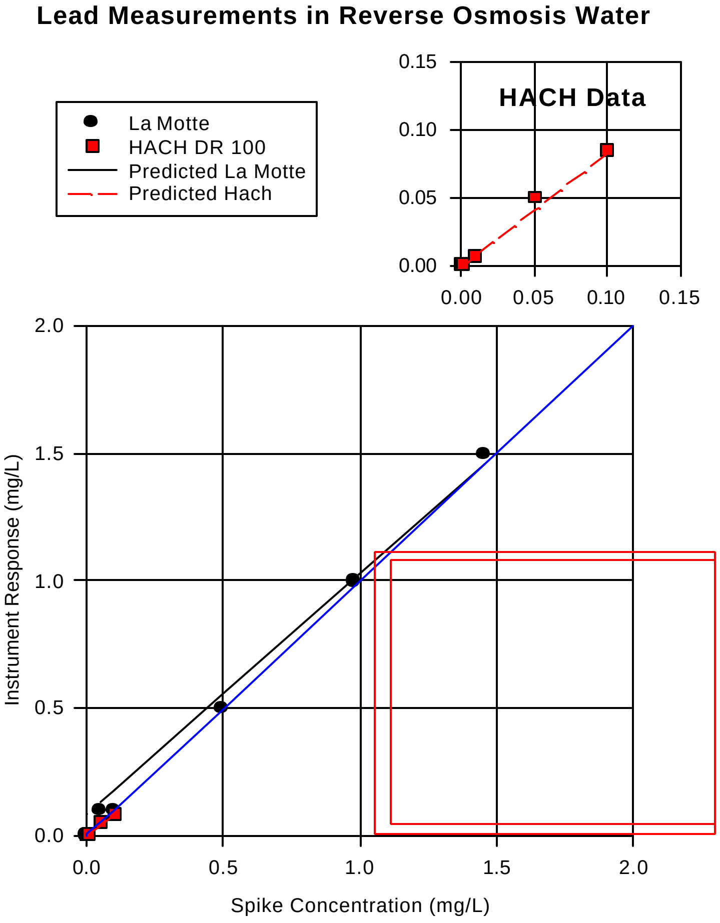


Figure 1. Example response curves for lead tests

Laser Fluorescent Methods for Heavy Metal Analyses

A current NSF/EPSCoR grant allowed us to develop tunable color center laser spectroscopic techniques for detection of toxic pollutants. As part of this grant, one of the new atomic laser fluorescence set-ups developed was based on a state-of-the-art spectroscopic, detection and laser equipment: a 0.75 m spectrometer ARC-750 (Acton Research Corp.), intensified TE-cooled 256x1024 CCD camera (Princeton Instruments), fiber optic probe guide for signal transportation, atomizing furnace (Perkin Elmer), and tunable color-center laser. Detection levels of less than 1 µg/L (ppb) were observed with this instrument for iron, lead, and copper during the preliminary experiments.

Development of portable alexandrite-color center laser system for UV excitation of atomic transitions

Many intense atomic absorption lines are located in UV-visible spectral ranges. Therefore development of efficient narrowband lasers sources tunable in 200-400 nm spectral range is of great importance in laser atomic fluorescence spectroscopy. In our recent studies of LiF:F_2^{+**} color center lasers, we showed that the LiF:F_2^{+**} laser exhibits excellent photo- and thermostable operation at room temperature when pumped by the radiation of an alexandrite laser and can provide efficient high power lasing tunable in 800-1200 nm spectral range. These results allowed us to build a reliable LiF:F_2^{+**} -

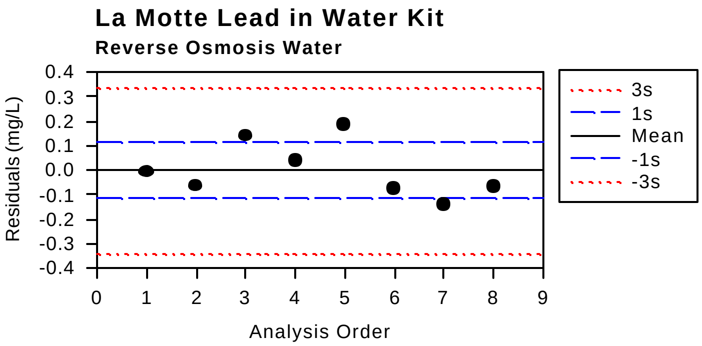


Figure 2. Residuals plot for lead test kit evaluation

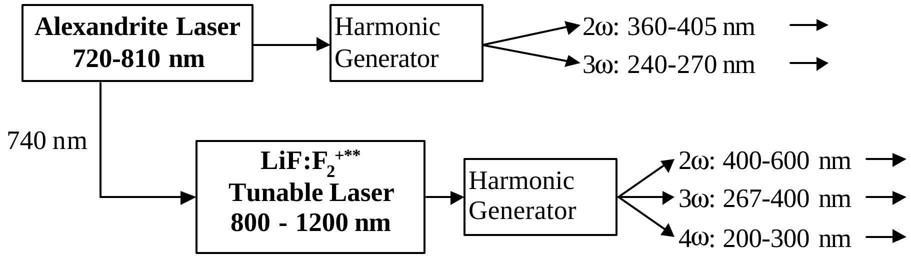


Figure 3. Block diagram of the laser system

alexandrite laser system which can be continuously tuned in 720-1200 nm range. The structure of the laser system is shown in Fig. 3.

The developed laser system consists of two lasers (Fig. 3):

- a pulsed alexandrite laser which can serve: 1) as a source of laser radiation tunable in the 720-800 nm range or 2) as a pumping source for a LiF:F_2^{+**} color center laser (in the latter case the output wavelength of the alexandrite laser is set at 740 nm, which is optimal for color center laser pumping);

- a LiF:F_2^{+**} color center laser tunable in the 800-1200 nm range. The conversion efficiency for the LiF:F_2^{+**} laser with a dispersive resonator is about 18-20% at the maximum of the tuning curve.

The combined fundamental tuning range of this system is from 720 nm to 1200 nm. The application of nonlinear crystals for harmonic generation allows for production of tunable laser radiation in the UV-Visible regions and continuously cover the 200-600 nm spectral range. (see Fig.3 and Table 2).

Table 2. Available Spectral Ranges for the LiF:F_2^{+**} -Alexandrite Laser System

Laser type	Fundamental	Second Harmonic	3rd harmonic	4th harmonic
Alexandrite laser	720-810 nm	360-405 nm	240-267 nm	180-200

F_2^{+**} color center laser	800-1200 nm	400-600 nm	270-400 nm	200-300 nm

Laser atomic fluorescence (LAF) analysis of copper and iron with graphite furnace atomizer

a) Cu atoms (Cu I)

The strong absorption transition $^2S_{1/2}$ ($3d^{10}4s$) -> $^2P_{3/2}$ ($3d^{10}4p$) at 324.754 nm was used for selective excitation of the $^2P_{3/2}$ level of Cu. The fluorescence signal was detected at the emission transition $^2P_{3/2}$ -> $^2D_{5/2}$ ($3d^94s^2$) at 510.554 nm.

The average power of the excitation beam was 10 mW at 324.754 nm (see Fig. 3 and Table 2). The repetition rate of the laser was 20 Hz and the pulse duration was about 50 ns. Spectral resolution of the spectrometer during the experiments was about 0.1 nm. Spectrum accumulation time was set to 5 sec (slightly less than the atomization time set by the graphite furnace controller), which allowed for signal collection during approximately 100 laser excitation pulses.

Typical examples of the observed fluorescence spectra for water solutions with different concentrations of Cu are shown in Fig. 4. All three spectra were measured under the same experimental conditions. The graphite furnace was heated to 2800-3000° C before and between measurements, in order to clean the graphite tube from possible residuals. The preliminary detection limit for Cu (for the RO water analysis) is seen to be << 1 µg/L.

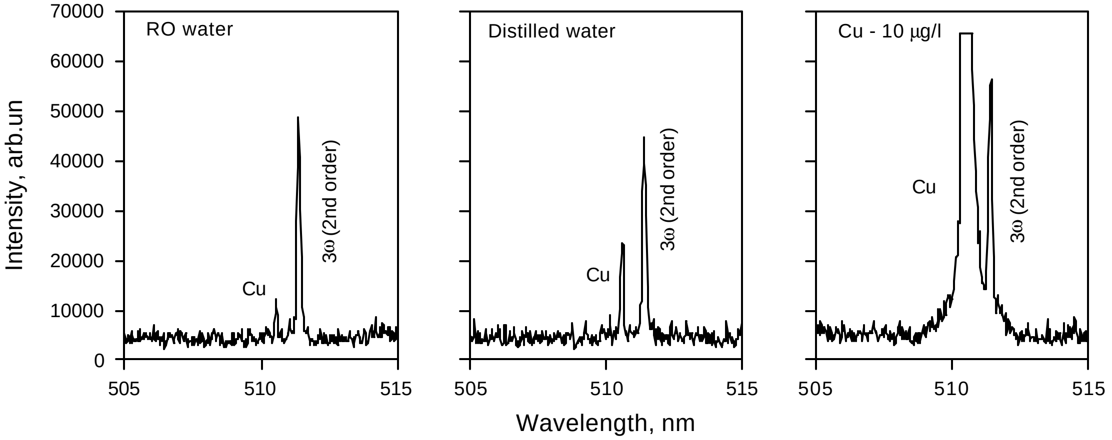


Figure 4. Fluorescence of Cu atoms under 324.75 nm laser excitation.

The spectral peak at 511.46 nm is due to some scattered light of the 3rd harmonic (255.73 nm) of alexandrite laser in the 2nd diffraction order. This peak is reasonably constant during the experiment, so we decided to leave it as a good amplitude reference signal, as indicated in Fig. 4.

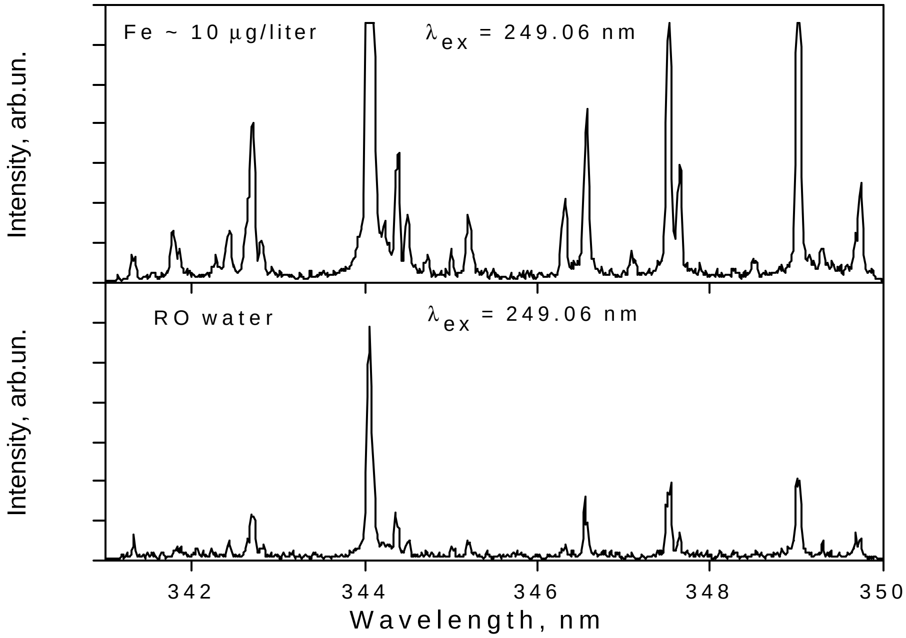
b) Fe atoms (Fe I)

Similar experiments were performed with Fe in water samples. Figure 5 shows spectral response for Fe at the 10 µg/L level, compared to RO water. The low iron concentration produced significant fluorescence peaks in the sample, especially at about 344 nm. It is also obvious that the very pure RO water also has some detectable iron.

As one can see, we were able to detect extremely low levels of Cu and Fe atoms, even in the RO and distilled water samples. It indicates that due to extremely good sensitivity of this instrumentation, special clean room conditions should be maintained in order to evaluate the detection limits of the installation and correctly measure the lowest impurity levels possible.

Development of LAF spectrometer with laser ablation atomizer

The main goal of this set of experiments was to develop a relatively simple atomizer based on the complete laser ablation of the sample. For this purpose, we designed and built a special optical chamber shown in Fig.6. The chamber has several optical windows. The principle of operation is as follows. A pulsed laser with a high energy per pulse (> 20 mJ) is focused onto the sample in the chamber. Due to laser ablation, the sample is vaporized and atomized. The UV excitation beam selectively tuned to the wavelength of the strongest absorption of the impurity of interest is introduced into the chamber through the second window. The fluorescence light is collected with a lens and directed into the detection system through an optical fiber. A slow flow of Argon through the chamber is maintained to prevent sample condensation on the optical windows.



* - all experimental conditions were
the same during both experiments

Figure 5. Fe I response in sample water

We attempted to determine the optimum operation parameters for the installation during our preliminary experiments. The parameters of interest were:

- optimum energy per pulse and focusing conditions for the ablation beam,
- optimum delay between the UV excitation and ablation pulses,
- optimum operation of the gated detection system (gate width and gate delay).
- optimum sample preparation.

Standard solutions with Cu and Fe were used in the test experiments. This experimental set-up offers the following advantages:

- both qualitative and quantitative analysis can be conducted since the intensity of spontaneous Raman spectra is linearly proportional to the concentration of the components
- applicable without sample preparation to liquids, solids or multiphase samples
- fully compatible with remote fluorescent measurements using the same equipment
- “real time” control and monitoring of chemical reactions and processes

- practically no limitations on the various conditions of: pressure, temperature, high electric or magnetic fields, radioactive materials, hostile or toxic environments

Development of LAF spectrometer with laser ablation atomizer (liquid samples).

The main goal of this experimental set-up was to develop a relatively simple atomizer based on the laser ablation of the sample. We designed and built a continuous flow nebulazier with laser plasma excitation, as shown on Fig.7.

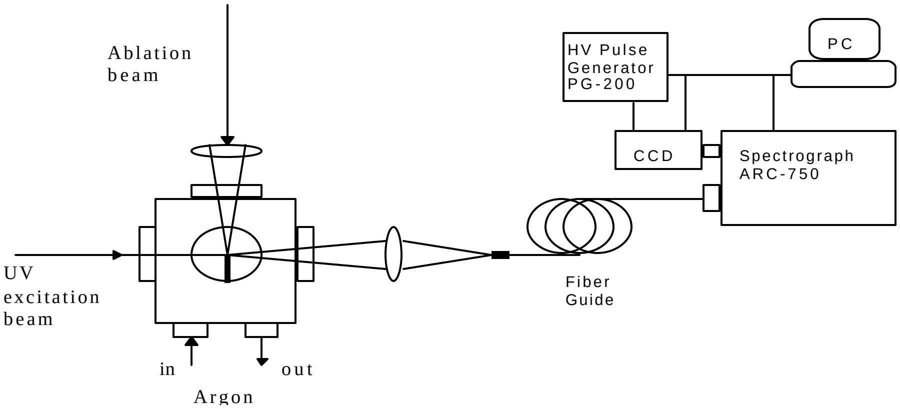


Figure 6. Experimental set-up for laser atomic fluorescence with laser ablation

The principle of operation is as follows. Argon gas flow and liquid sample are introduced into a nebulizer. Small amounts of the liquid sample is drawn into the nebulizer by the Argon flow. This gas and sample mixture exits the nebulizer through a conical nozzle having a diameter of 1 mm. A pulsed laser beam having high energy per pulse (20-100 mJ, repetition rate - 10 Hz) is focused onto the exiting jet of the sample and gas mixture at the exit from the nebulizer nozzle. The energy per pulse and the focal distance of the focusing lens are chosen in such a way that optical breakdown occurs in the mixture jet at ~ 1-2 mm above the nozzle, generating a laser plasma plume. Due to the laser plasma generation, the sample droplets are vaporized, atomized and ionized. The fluorescence light is then collected with a lens and directed into the detection system through an optical fiber.

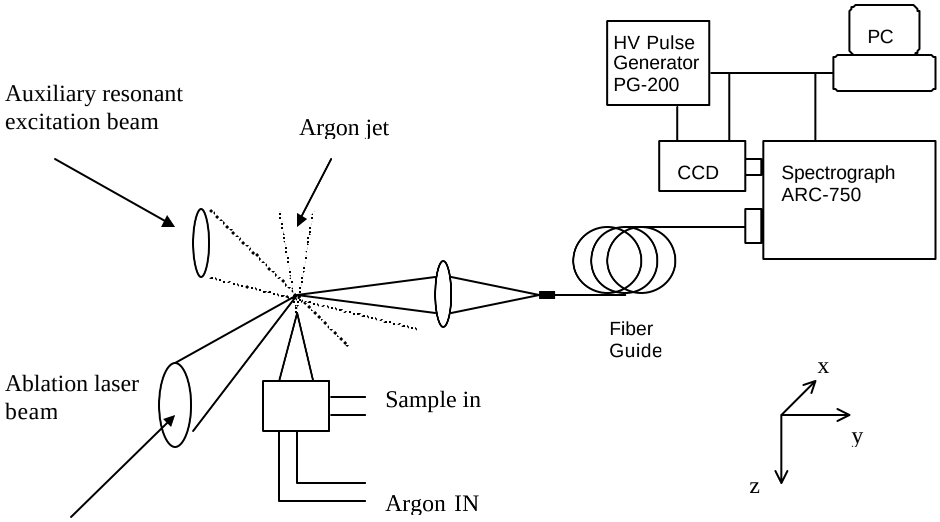


Figure 7. Experimental set-up for laser atomic fluorescence with laser ablation

We ran initial tests to determine the optimum operation parameters for this installation. Parameters of interest included:

- optimum energy per pulse and focusing conditions for the ablation beam, optimum operation of the gated detection system (gate width and gate delay), and detection limits.

Standard solutions with Na, Cu and Fe were used in test experiments. The laser plasma occurring due to optical breakdown in Ar jet acts as a strong excitation source which allows it to atomize and ionize the sample particles. Consequently, it is possible to observe the self-fluorescence of the impurity atoms present in the sample. This fluorescence is observed during the relaxation of the plasma plume generated by a short laser pulse. Usually this time interval is about 0-10 µs.

The detection limits for this installation were estimated to be about 1 ppm (1 mg/L). The upper limit of the linear range of fluorescence versus concentration was about 2000 mg/L. The sensitivity can be increased by introducing an additional low power/energy UV excitation beam which is selectively tuned to the wavelength of the strongest absorption of the impurity of interest.

Laser Breakdown Spectroscopy of Liquid Samples

Aluminum (Al)

For aluminum, the fluorescence signals at 394.4006 nm and 396.1520 nm were used. This emission transition was $^{2}S_{1/2}$ $(3s^{2}4s)$ -> $^{2}P^{0}_{1/2}$ $(3s^{2}3p)$ for 394.4006nm. The emission transition for 396.1520 nm was $^{2}S_{1/2}$ $(3s^{2}4s)$ -> $^{2}P^{0}_{3/2}$ $(3s^{2}3p)$. The gate delay and width were optimized for best results to 15µs and 500µs respectively. With the single laser system, the detection limit of Aluminum was approximately 30 ppm (Fig.8).

Cadmium (Cd)

The optimum gate delay and width for cadmium were 2µs and 250µs respectively. The fluorescence signal at 228.8022 nm was used. The limits of detection for cadmium in this system were approximately 30 ppm (Fig.8).

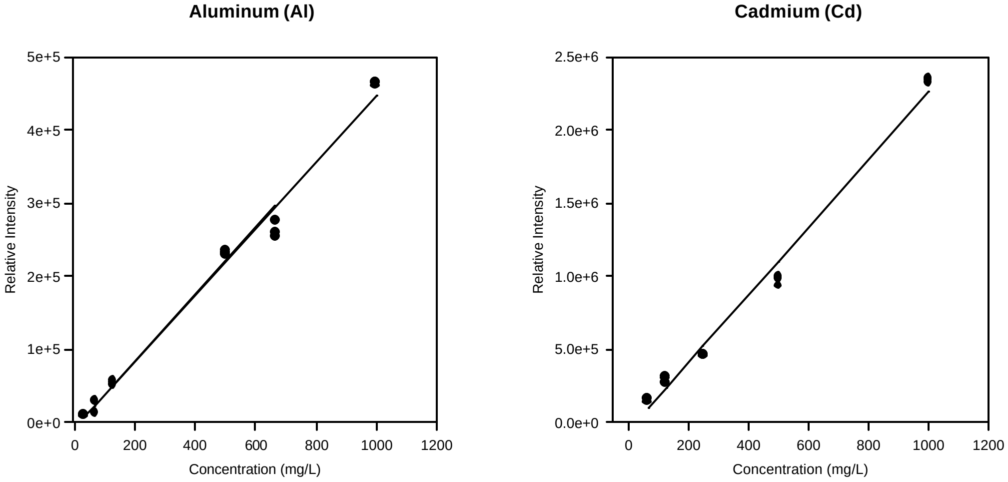


Figure 8 : Aluminum and Cadmium

Copper (Cu)

The copper fluorescence signals were detected at 327.3957 nm as well as at 324.754 nm. The gate delay was optimized at 15µs and the gate width at 35µs. Copper had a detection limit of 3 ppm (Fig.9). The emission transition of copper detected at 324.754 nm was $^{2}P^{0}_{3/2}$ $(3d^{10}4p)$ -> $^{2}S_{1/2}$ $(3d^{10}4s)$. The emission transition detected at 327.3957 nm was $^{2}P^{0}_{1/2}$ $(3d^{10}4p)$ -> $^{2}S_{1/2}$ $(3d^{10}4s)$.

Iron (Fe)

Iron had an optimized gate delay and gate width of 24µs and 30µs respectively. Iron was the most interesting element of this experiment in that it was detected at four wavelengths. Those wavelengths were 248.32718, 250.1132, 252.28505, and 256.6901 nm. Iron had a detection limit of approximately 30 ppm (Fig.9). The emission detected at 248.32718 nm was $^{5}F^{0}_{5}$ -> $^{5}_{a}D_{4}$ $(3d^{6}4s^{2})$. The emission detected at 250.1132 nm was $^{7}P^{0}_{3}$ -> $^{5}_{a}D_{4}$ $(3d^{6}4s^{2})$. The transition at 252.28505 nm was found to be $^{5}_{x}D^{0}_{3}$ -> $^{5}_{a}D_{4}$ $(3d^{6}4s^{2})$. The last transition at 256.6901 was found to be $^{5}_{x}D^{o}_{4}$ -> $^{5}_{a}D_{4}$ $(3d^{6}4s^{2})$.

Lead (Pb)

Lead was detected at 405.7807 nm with a gate delay of 25µs and a gate width of 50µs. Lead's limit of detection was found to be about 30 ppm (Fig.10). The transition of lead was shown to be $^3P^0_1$ (6p7s) -> $^3P_2$ ($6p^2$).

Sodium (Na)

Sodium was the first element investigated in this experiment. It was used to help initially setup the system and was later used as a reference point so that the equipment could be tested to see that it was in proper working order. Sodium was detected at two wavelengths, 589.59236 and 588.99504 nm. The detection limit for sodium was 2.0 ppm, the best results of all elements during this experiment. The transition at 588.99504 nm was one of $^2P^0_{3/2}$ ($2p^6$3p) -> $^2S_{1/2}$ ($2p^6$3s). The transition at 589.59236 nm was $^2P^0_{1/2}$ ($2p^6$3p) -> $^2S_{1/2}$ ($2p^6$3s).

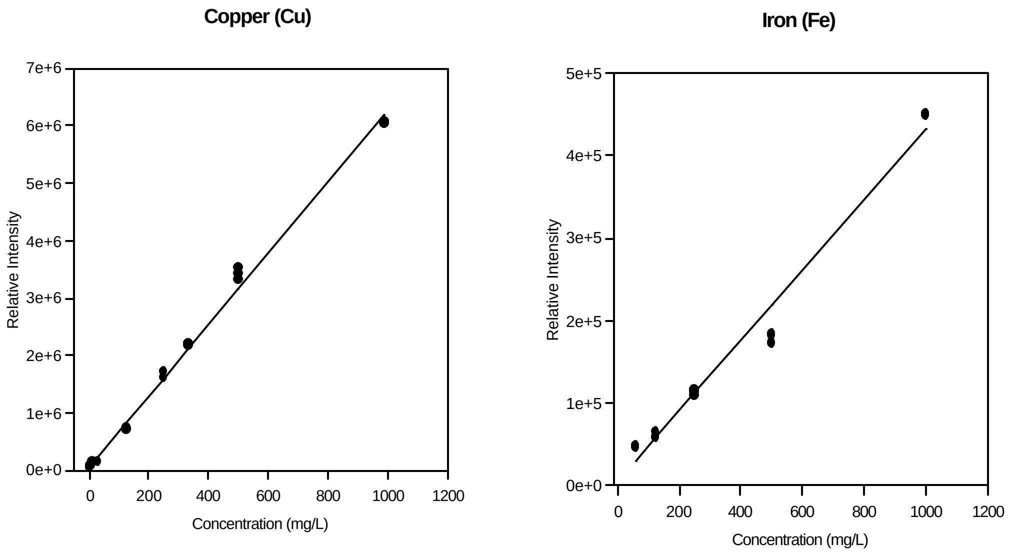


Figure 9 : Copper and Iron

Zinc (Zn)

Zinc had an optimized gate delay and width of 10µs and 1µs respectively. Zinc was detected at 213.856 nm. This element had a detection limit of 30 ppm (Fig.10). Both clean and dirty matrix samples of zinc were examined, with both having approximately the same spectra and the same detection limits. This is especially important because it shows that the plasma generation system is not dependent on the sample's preparation. Therefore, no special preparation of a sample is necessary to detect heavy metals in this plasma generation system. Many other single laser systems must have the sample prepared before analyses can begin.

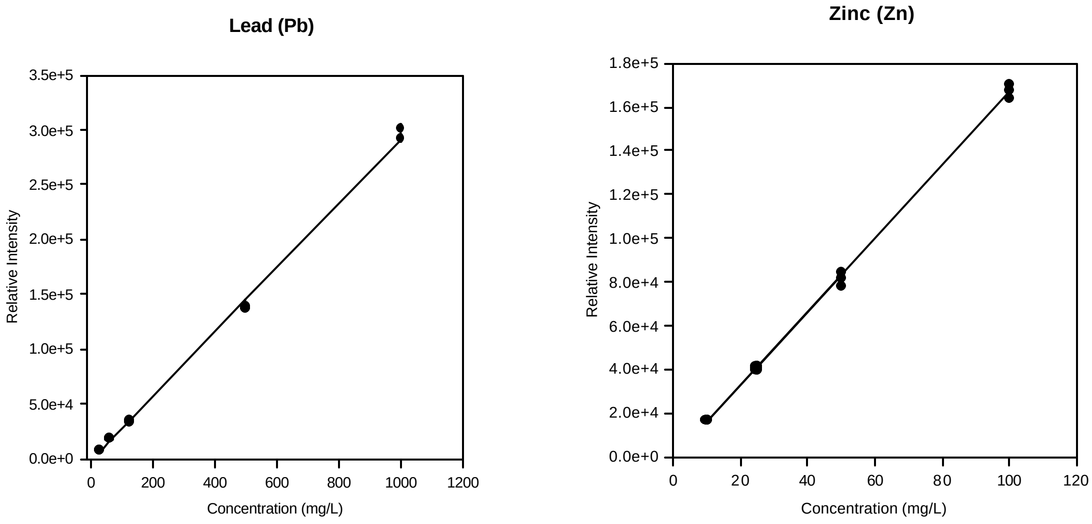


Figure 10 Lead and Zinc

Conclusion

LAF testing of water samples containing heavy metal atoms were compared with results using atomic absorption spectrophotometry. Initial indications showed good agreement between these two methods. Detection levels of less than 1 ppb were observed for iron, lead, and copper during these preliminary experiments using our laser atomic fluorescence instrumentation. We expect that optimization of our experimental set-up for fluorescence analysis of atomic spectra will allow us to improve these very low levels of detection by several orders of magnitude.

Laser plasma occurring due to optical breakdown in Ar jet acts as a strong excitation source which atomizes and ionizes the sample particles and consequently allows the observation of the self-fluorescence of the impurity atoms present in the sample. The detection limits for this installation were estimated to be about 1 ppm. The linear dependence of fluorescence intensity versus concentration of impurities was observed to be over a very large dynamic range of up to 2000 mg/L.

We demonstrated a novel tunable solid state LiF:F_2^{+**} -alexandrite laser system which provides the possibility for selective laser excitation that is continuously tunable in the 200-600 nm range. The LAF spectrometer was based on a state-of-the-art spectroscopic, detector and laser equipment. This experimental set up can serve as a prototype to design a portable spectroscopic set-up for field operations having very low detection limits, a wide dynamic range, and minimal sample preparation requirements. Inexpensive and fast instrumentation, especially if used *in-situ*, will vastly improve environmental research and characterization efforts by enabling greatly increased sample numbers with better spatial and temporal resolution. Laser-based instrumentation may significantly reduce the cost of very sensitive simultaneous analyses of heavy metals, with sample preparation efforts, and offer a variety of options for different sample types.

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