

ELEMENTAL IDENTIFICATION OF LITHIUM IN CLANDESTINE
LABORATORY CASEWORK BY ATOMIC EMISSION SPECTROSCOPY

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ABSTRACT

The conclusive identification of lithium in clandestine laboratory samples may help the analyst determine the manufacturing method used in a case, relate samples to other investigative information in a case, or assist in assessing the significance of items found in a case. Herein we discuss the application of atomic emission spectroscopy to the identification of lithium in clandestine laboratory casework. A brief discussion of the theory and instrumentation required to conduct atomic spectroscopy is presented, followed by an example atomic emission spectroscopy method, including an overview of its validation.

SUMMARY OF PROBLEM

The dissolving metal reduction of pseudoephedrine or ephedrine using ammonia and an alkali metal has been one of the most common methods of methamphetamine manufacture for a decade. While several alkali and alkali earth metals have been shown to be useful in accomplishing this reduction [1], the ready availability of lithium in batteries has made it by far the most commonly used metal in clandestine laboratories. Several other clandestine laboratory syntheses employ reagents where lithium is present as a cation including lithium aluminum hydride and phenyl lithium.

The identification of lithium in clandestine laboratory samples may provide information on the identity and relevance of items found at a site, relate samples to other investigative information (receipts, informants' reports, etc.), or help the analyst determine the manufacturing method used at a site. Despite the benefits of identifying lithium in casework, many laboratories and analysts are only able to report it with a qualified conclusion (e.g. "indications of" or "consistent with").

The lack of confidence in lithium analysis seems to, in many cases, stem from an expectation in many laboratory systems that chemists use instrumental methods to provide 'reviewable' data. This, coupled with the lack of suitable instrumentation, prevents many laboratories from reporting definitive identifications.

A wide variety of techniques are available for the identification of lithium in clandestine laboratory casework including tests of the reactivity of metal samples with water, a spot test [2-4], crystal tests [4-6], a flame test [4], infrared spectroscopy [7], and capillary electrophoresis [8]. X-ray fluorescence (XRF) and energy dispersive x-ray (EDX) are not suitable for direct analysis of lithium [9], though they can be used to eliminate interferants for other analytical methods (e.g. strontium as an interferant in flame tests).

Herein we provide background on atomic emission spectroscopy as a suitable, definitive instrumental method not commonly used in forensic science and describe an approach to validating an atomic spectrometer for use by criminalists in clandestine laboratory sample analysis.

ATOMIC SPECTROSCOPY

Atomic absorption spectroscopy (AAS) and atomic emission spectroscopy (AES) are two of the most definitive and widely accepted approaches for the identification and quantification of lithium. AES operates on the same scientific principles as the flame test commonly used as a part of lithium analysis, but uses more sensitive and specific equipment to characterize the emitted UV-visible light.

Like molecular UV-Vis spectroscopy, atomic spectroscopy looks at the electronic transitions of valance electrons. Like molecular spectroscopy, the energy of these transitions can be monitored by absorption, emission, or fluorescence. The absorption, emission, and fluorescence spectra of molecules are relatively broad and non-specific with peak widths between several and several hundred nanometers. In contrast, once all bonding interactions are eliminated during the atomization process, the energies of valance electrons depend only on the charge of the nucleus. These electronic transitions result in sharp (widths typically of 0.01 nm) element specific bands.

Atomic spectrometers employ special sample chambers, referred to as atom reservoirs, to generate the atomized sample required for analysis. Several techniques are available to atomize samples including flames and plasma torches. Flame spectroscopy instruments were at one time the most common, but as the cost of inductively coupled plasma (ICP) instruments drops, they are

Table 1: Common Flame Temperatures.

Fuel	Oxidant	Temperature	Ref.
CH ₄	Air	1700-1900 C	11
CH ₄	O ₂	2700-2800 C	11
H ₂	Air	2000-2100 C	11, 12
H ₂	O ₂	2550-2700 C	11, 12
C ₂ H ₂	Air	2100-2400 C	11, 12
C ₂ H ₂	O ₂	3050-3150 C	11, 12
C ₂ H ₂	NO ₂	2600-2800 C	11, 12
Inductively Coupled Plasma		6,000-10,000 C	12

becoming the method of choice for many applications, especially quantitative analysis and multi-element analysis, due to their increased stability and sensitivity, long linear dynamic range, and reduced chemical interference effects.

These atom reservoirs add energy, typically as heat, to the sample until molecular species are eliminated and the desired atom or excited atom is present in the gas phase for analysis (Figure 1). In the first step of this process for a flame or ICP instrument, the aqueous sample passes through a nebulizer (Figure 1, inset) to produce an aerosol of very fine drops that will allow efficient and stable atomization. The first energy absorbed by the nebulized sample entering the flame or plasma results in desolvation producing a solid sample (M(s)). During this process reactions may occur in the electron rich flame environment including the formation of oxides and capture of electrons by ions. The dried particles are then volatilized by first melting and then passing into a gaseous state (M(g)). Molecules may then dissociate to form gaseous atoms (A(g)) and then ionize (A+(g)) if sufficient energy is present. Excited states of molecules, atoms, and ions may form as intermediates in the dissociation or ionization process or simply as separate species. The relative population of each species depends on the flame or plasma temperature and the energy levels for the species.

The higher the flame temperature (Table 1), the further the analyte will progress along the excitation pathway and the higher the relative population of higher energy species (down and to the right on Figure 1). Flame temperatures that are too low can result in interferences from molecular species. Flame temperatures that are too high can result in a drop in sensitivity due to depletion of the population of the atomic state being studied, though this is more of a concern for atomic absorption than atomic emission spectroscopy.

The relatively low excitation energies for lithium allow the formation of high populations of excited atoms and strong emission intensity, even in relatively low temperature flames including natural gas and air flames (1700–1900 °C), making AES practical using most instruments and flames. The atomic emission lines

of lithium at 671, 610, and 548 nm [10] result in the red flame used as the diagnostic result in the conventional lithium flame test. The observation of these emission lines (narrow peaks) in a low temperature flame is specific for lithium because the energies of the transitions are determined by the charge of the nucleus and also because few elements have excitation energies as low as lithium and, as a result, do not have significant emission intensity in low temperature flames.

A wide variety of detector configurations are used in commercial atomic spectrometers. Many instruments are equipped with a single wavelength detector (a monochromator that does not scan) used primarily for quantitative analysis of a single known element. Other instruments contain multiple single wavelength detectors or a scanning detector capable of analyzing multiple elements simultaneously. The ability of wavelength scanning instruments to simultaneously look for multiple bands and multiple elements make them preferable for the qualitative analysis of clandestine laboratory samples, but with proper controls a single wavelength instrument can provide the definitive identification

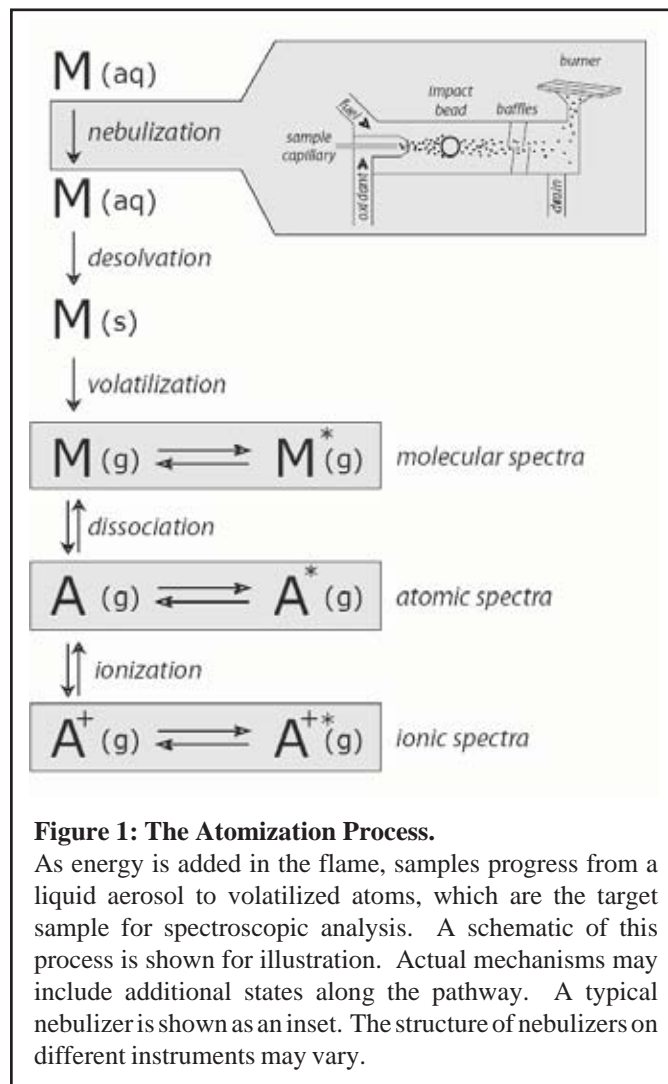


Figure 1: The Atomization Process.

As energy is added in the flame, samples progress from a liquid aerosol to volatilized atoms, which are the target sample for spectroscopic analysis. A schematic of this process is shown for illustration. Actual mechanisms may include additional states along the pathway. A typical nebulizer is shown as an inset. The structure of nebulizers on different instruments may vary.

Ion	Color	Intensity
Li	Red	0.935
Sr	Red	0.074
Mn	Lt. Yellow	0.001
Ba	Green	0.001
Ca	Orange	0.001
Cd	--	0.001
Na	Orange	0.000
Mg	--	0.000
K	--	0.000
Cs	--	0.000
I	--	0.000

Table 2: Select Cation Emission Intensities at 671 nm.

All ions are measured as 1000 ppm solutions. The intensity scale was first normalized to 1.000 using the 1000 ppm lithium. Strontium yielded the strongest emission intensity of an element other than lithium. Ions were selected based on their likelihood of being found in clandestine laboratory samples or based on published atomic lines near 671 nm taken from the CRC Handbook of Chemistry and Physics.

of lithium in these samples. The remainder of this paper discusses an approach to the validation of a single wavelength atomic spectrometer for the analysis of lithium in clandestine laboratory samples.

AN ATOMIC EMISSION SPECTROSCOPY METHOD FOR LITHIUM ANALYSIS

Overview

This method has been developed using the Fresno State Chemistry Department's GBC 902 Atomic Absorption Spectrometer operating in the emission mode. After the instrument is set to the emission line of lithium using a standard solution, the unknown sample, prepared by drying and then volumetric dilution in water, is aspirated into the flame. The appearance of the flame is noted and the emission intensity at 671 nm (lithium's strongest emission) is recorded. Subsequently, the emission intensity is measured for a standard solution of strontium, which was observed to have the strongest emission of the 11 elements tested during validation, when the instrument was set to the lithium band at 671 nm. If the emission intensity of the sample at 671 nm is greater than the maximum interferant signal, then lithium is present in the sample.

On this instrument, this protocol allows identification of lithium down to two percent by weight of the total dissolved solids of a sample.

Example Protocol

Instrumentation

This protocol was developed using a GBC Scientific Equipment 902 Double Beam Atomic Absorption Spectrophotometer set in emission mode. This instrument is configured with a 10 cm premix burner and utilizes an air-acetylene flame. The monochromator has a minimum slit width of 0.2 nm and has manual wavelength adjustment.

Analysis

1. A working solution of the unknown samples is prepared by measuring the dry weight of the sample and diluting to a final concentration of 1.0 mg/mL or 1000 ppm with deionized or distilled water.
2. 1000 ppm stock solutions of sodium, lithium, and strontium are prepared by diluting a sodium salt (e.g. 0.2542 grams of sodium chloride), a lithium salt (e.g. 0.6108 gram of lithium chloride), or a strontium salt (e.g. 0.6108 gram of strontium nitrate) to 100.0 mL with deionized or distilled water. The 10 ppm lithium calibration solution and 10 ppm strontium interferant solutions are then prepared by diluting 1.00 mL of the 1000 ppm lithium and strontium to 100.0 mL with the ionization suppression solution (1000 ppm sodium solution). Each of these solutions may be retained as stock solutions for repeated use.
3. The analysis solution of 0.010 mg/mL or 10 ppm of the unknown sample and blank sample are prepared by diluting 1.00 mL of the working solution from step 1 and 1.00 mL of the water used to prepare the working solution to a final volume of 100.0 mL with the ionization suppression solution (1000 ppm sodium solution from step 2).
4. The instrument is turned on and configured for emission analysis. The minimum instrument slit width of 0.2 nm is selected to minimize interferences and the coarse wavelength is set to approximately 671 nm. The flame is ignited and the fuel mix is set to provide a stoichiometric to slightly fuel lean flame. The instrument is set to average signal over 5 seconds.
5. A 10.0 ppm lithium standard solution (0.100 gram LiCl in 100.00 mL of distilled or deionized water), prepared by diluting 1.00 mL of a 1000 ppm standard to 100.0 mL with the 1000 ppm sodium solution described above, is aspirated and the wavelength of the detector is set by maximizing the observed emission intensity. This is essentially wavelength calibration of the instrument using the sharp lithium emission band. The burner orientation and position are set to maximize the observed emission intensity.
6. The instrument's 1.000 intensity level is set using this 10.0 ppm lithium solution. Note that this intensity could only be achieved using elemental lithium given the prescribed dilution scheme.
7. Deionized or distilled water is aspirated and the instruments zero level is set after the signal stabilizes.

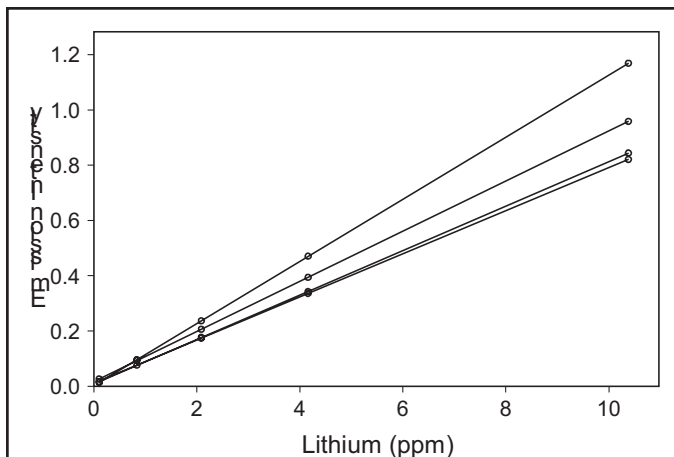


Figure 2: Lithium Calibration Curves.

Direct calibration curves were generated with increasing concentrations of lithium chloride with sodium chloride as an ionization suppressor. Replicate curves from four separate days over one month differ slightly in the sensitivity (slope), but all show good linearity and consistent relative response of lithium and strontium.

8. A 10.0 ppm strontium standard solution ($\text{Sr}(\text{NO}_3)_2$ in distilled or deionized water), also containing 1000 ppm sodium, is aspirated and the observed emission intensity is recorded. The measured value should be 0.004 ± 0.003 units (set to 1.000 as maximum).
9. The blank is aspirated and the observed emission intensity is recorded after the signal stabilizes.
10. The 10.0 ppm sample solution is aspirated and the observed emission intensity is recorded after the signal stabilizes. The flame should appear orange. If a yellow to white color is observed, the sample has too much organic content (e.g. solvent) to allow definitive identification without additional controls.
11. Repeat steps 8–10 three times to provide meaningful statistics.
12. The mean blank reading should not be significantly different from zero as evaluated by a t-test (generally 0.000 ± 0.003 intensity units). If the instrument has been properly zeroed, a larger blank signal would be indicative of an impurity of water used for sample preparation. As emission is linear in this concentration range, it may be corrected by subtracting the mean blank signal from each sample measurement, if laboratory procedures allow this type of correction.
13. Perform a t-test comparing sample means to determine if the lithium intensity is significantly higher than the strontium intensity at a 99.9% confidence limit. The TTEST() function in Microsoft Excel can perform this calculation for you, or you can find details in most analytical chemistry or statistics text books.

14. Additional replicate measurements (e.g. 5 or 7 total) may be required to distinguish dilute lithium samples (signals of less than approximately 0.013 intensity units) from interferants with statistical significance.

It should be noted that the flame color for this protocol will be dominated by the orange emission of the sodium used as an ionization suppression agent, so the characteristic red color may not be observed. For this protocol we have selected the 99.9% confidence limit, though any other confidence limit could be selected based on preferences of the individual laboratory. The 99.9% confidence limit recommended above should not be interpreted as directly meaning that there is a 0.1% possibility of a false positive. First, the calculated t-value may be considerably above this threshold. In this case the calculated p-value may be useful in assessing the potential for false positives. Second, the tested interferant signal represents the maximum possible signal if your sample were pure strontium metal and any salt would have a considerably lower interferant concentration.

METHOD VALIDATION

A general description of the validation performed on the GBC Scientific Equipment 902 Double Beam Atomic Absorption Spectrophotometer set in emission mode is discussed below.

Linear Range

The effective linear dynamic range of the instrument for the analysis of the lithium 671 nm band was evaluated with standard lithium solutions from 0.1 to 1000 ppm. Each of these standard solutions was prepared from lithium chloride using Class A volumetric glassware. The instrument range was set using both 1000 and 10 ppm solutions in separate experiments. In each case the instrument response showed negative curvature, with the lower concentration range of 0.1 to 10 ppm showing the greatest linearity.

The linearity in this region was significantly improved by the addition of sodium chloride as an ionization suppressing agent. Lithium calibration standard solutions were prepared from 100x stock solutions of lithium chloride in distilled, deionized water. The calibration standards were prepared by dilution of these stock solutions with 1000 ppm sodium (NaCl). The addition of sodium chloride did not interfere with the lithium signal, as no emission intensity was observed in the absence of added lithium. The addition of sodium chloride yielded a calibration curve with a linear response from 0.1 to 10 ppm (Figure 2).

At 10 ppm the red color of lithium is not visibly apparent in the flame, particularly with the added sodium. Using a shorter flame, either by turning or replacing the burner, may allow higher concentration solutions to fall in the dynamic linear range or could allow the red color to be observed visually if sodium was not used as an ionization suppressor. This protocol allows use of the working 1000 ppm solution of the sample to check flame color if desired.

Specificity

The specificity of the single wavelength atomic emission analysis for lithium was evaluated by testing a variety of inorganic and organic interferants.

The ability of the instrument to resolve lithium's 671 nm emission line from those of other elements was evaluated by testing common inorganic clandestine laboratory species and elements with known atomic absorption lines in the vicinity of 671 nm. A 1000 ppm lithium standard solution was used to set the wavelength to the 671 line and to set the 1.000 signal intensity. These species were screened as 1000 ppm solutions. Of these solutions, only strontium gave significant emission intensity (Table 2). Note that the observed intensities are not on the same scale as the lithium analysis results described above using 10 ppm lithium to set the instrument range.

Residual organic solvents have the potential to produce broad molecular emissions when added to a flame, causing potential spectral interference. To assess whether residual organics may interfere with analysis, solutions containing ethanol were analyzed. Absolute ethanol was diluted with the 1000 ppm sodium chloride stock solution to an ethanol concentration of 10% v/v. A blank sample was diluted with the 1000 ppm sodium chloride and the 10% ethanol in sodium chloride. The resulting intensities, 0.000 and 0.016, showed only a moderate increase in observed signal intensity despite a very bright (uncomfortable to look at) white-yellow flame. If no change in the flame appearance is observed (white-yellow instead of orange), it is concluded that there is negligible organic interference at 671 nm.

pH Sensitivity

Most clandestine laboratory samples from lithium-ammonia cooks are strongly alkaline containing lithium and/or ammonium hydroxide and carbonate salts. The sensitivity and dynamic range of the instrument for lithium was evaluated in the presence of sodium hydroxide and ammonium hydroxide to determine if alkaline solutions that may be encountered in methamphetamine laboratory samples would affect the results of the test.

Stock solutions ranging between 10 and 1000 ppm lithium (LiCl) were diluted with 1000 ppm sodium hydroxide, 1000 ppm ammonium hydroxide, and 1000 ppm sodium chloride. The resulting solutions were tested and no significant differences were observed for the sensitivity or dynamic range for lithium. Based on the prescribed dilution scheme, the sample concentration of hydroxide will be much lower (10 ppm or less) in actual samples.

Reproducibility

The reproducibility of this method was assessed by rerunning a 10 ppm strontium standard solution and the 0.1 through 10.0 ppm lithium in 1000 ppm sodium chloride standard described above on four days ranging over one month. Because the instrument was in frequent use by analytical chemistry classes during this period, these experiments evaluate the ability of the setup protocol to produce consistent results.

	A	B	C	D	E	F
1		Replicate Intensity Measurements normalized to 10 ppm Li (1.000)				Documentation
2						B3:D5 = data
3	Sr (10ppm)	0.003	0.003	0.004		C7 = user entered
4	Blank	-0.002	-0.001	0		B10=AVERAGE(B4:D4)
5	Unknown	0.043	0.044	0.043		B11=STDEV(B4:D4)
6						D10=COUNT(B4:D4)
7	Confidence Level		99.9%			B12=ABS(B10)*SQRT(D10)/B11
8						D12=TINV(1-C7,D10-1)
9						C16=TTEST(B3:D3,B5:D5,1,3)
10						C17=1-C7
11	Mean	-0.001	N	3		
12	ST Dev	0.001				
13	t calc		1.73	t crit	31.6	
14	Conclusion:	no significant difference from 0				
15						
16						
17						
18	Conclusion:	Unknown is significantly higher than Sr				
19	Conclusion:	Lithium is present in the sample				

Figure 3: Statistical Analysis of Lithium Reaction Sample Results Using Excel.

The data from analysis of the lithium reaction sample using the described procedure is shown in cells B3:D5. There was no statistically significant difference at the 99.9% confidence limit ($p=0.23$) between the measured blank values using a Student's t-test for comparison with a known value (equation from Harris, Quantitative Chemical Analysis). The measured value for the unknown was significantly greater than the strontium reference at a 99.9% confidence limit ($p=6 \cdot 10^{-8}$) as determined using a Student's t-test assuming unequal variances (function in Excel). Because the observed signal was significantly higher than the maximum possible interferant signal it is concluded that lithium is present in the sample.

Moderate differences in the sensitivity of the instrument (slope of the lithium calibration curve) were observed (Figure 2), perhaps due to slight difference in the fuel/oxidant mixture. The observed differences in intensity affected the lithium and strontium samples similarly, so the ability of the method to distinguish lithium and strontium is reproducible.

Clandestine Laboratory Samples

Two real world test samples were taken from two methamphetamine manufacturing reactions conducted as part of training at the California Criminalistics Institute in September 2005. Samples were provided by Jerry Massetti (CCI) and Mark Kalchik (Cal DOJ Fresno). These samples were dried and a sample of the resulting sludge was weighed and diluted with water to give 1 mg/mL solutions. The sample was diluted to a final concentration of 0.010 mg/mL using a stock 1000 ppm sodium chloride solution.

The instrument response at 671 nm was calibrated using the standard 10 ppm lithium calibration solution and zeroed using blank water. Three replicate measurements of the blank as well as strontium and sample solutions were then taken. Statistical analysis of the data from the lithium reaction (Figure 3) shows a significant difference between the lithium reaction and the interferant at a 99.9% confidence level ($p = 1.15 \cdot 10^{-7}$). After

repeating this analysis on the sodium reaction, the measured signal was not significantly higher than that of the maximum interferant signal.

CONCLUSION

A variety of wet chemical tests and instrumental tests are available for the qualitative analysis of lithium in clandestine laboratory casework. The flame test routinely used in clandestine laboratory casework is a primitive form of atomic emission spectroscopy, whose specificity can be significantly improved using instrumentation to observe the sharp atomic emission bands of lithium. New atomic emission spectrometers can be purchased for approximately \$50,000, obtained used, or may be available for use at nearby private laboratories or academic institutions. A simple spectroscope offers a low cost alternative for observing the characteristic sharp atomic lines if an atomic emission spectrometer is not available for use.

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