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Determination of Trace Amounts of Lead in Water by Metastable Transfer Emission Spectrometry

Sir: We have previously reported the application of an analytical technique known as metastable transfer emission spectrometry (MTES) (1) to the detection of elements from solids (2, 3), gas phase alkyls and hydrides (4), and as a selective detector for hydrocarbons useful in gas chromatography (5). We now wish to report the application of this technique to the detection of trace metals in water. The MTES technique depends on the activation of fluorescence from the constituents of the sample by contact with active nitrogen in the gas phase. Thus, the liquid samples must be vaporized in a manner compatible with the detection and measurement of the resulting fluorescence. This is accomplished by staged heating of a tantalum receptacle containing the liquid sample.

When lead vapor is mixed with active nitrogen, a simple emission spectrum dominated by a few neutral Pb lines results. In the order of their relative intensities (uncorrected for detector response) these lines appear at 405.8, 280.2, 283.3, and 217.0 nm. The 280.2- and 283.3-nm lines are nearly equal in intensity. We have detected lead in aqueous solution by monitoring the 283.3-nm line and the 405.8-nm line.

Figure 1 shows a diagram of the apparatus. It is similar in design to the one employed for the detection of solid samples (2) except that the crucible has been replaced by a small tantalum boat. Samples are placed in the small depression in the metal boat and resistively heated by a Perkin-Elmer HGA-2100 graphite furnace power supply. The sample undergoes similar treatment to that used in furnace atomic absorption: drying to remove solvent and atomizing to vaporize the sample into the gas flow. Samples are treated to a 60-s drying cycle at 100 °C followed by a 20-s atomizing cycle at 1100 °C. No charring cycle is used since there are no organics present in the standard solution. The lower temperatures are calibrated with a thermocouple. Higher temperatures are calibrated with an optical pyrometer viewing through the quartz window at the top of the flow tube. Test runs are made with no liquid present to determine the intensity of the black-body emission from the hot boat and with samples of diluting solution to determine background levels. Active nitrogen is produced by metering in nitrogen gas at approximately 600 std cm³/min through a 12-mm quartz tube. The tube is enclosed in a McCarroll-type microwave cavity, and a microwave discharge is maintained by supplying 70–90 W from a Raytheon microwave generator. No lead signal is

observed when the generator is turned off. The signal increases with added power up to 80 W and remains constant as the power is increased from 80 to 100 W. An argon flush from the bottom also at approximately 600 std cm³/min serves to entrain the samples into the gas flow. The combined flows give a total system pressure of 2.6 Torr. The emission intensity from the atomic species of interest is monitored by tuning the monochromator to a wavelength previously determined to be suitable for MTES. A hollow cathode lead lamp serves as a convenient source for tuning the detection system.

The lead and blackbody signals were determined to be separated in time. Evidently the rate of increase of the temperature of the tantalum boat during the atomize cycle is sufficiently slow that the lead is evaporated (mp 327 °C) before the continuum emission becomes significant. At 1 ppm lead, the peak signal at 283.3 nm was ten times greater than the peak of the blackbody emission; they become comparable at less than 0.1 ppm. Effective baffling could easily improve this ratio by eliminating most of the scattered light from the hot tantalum boat. Our arrangement employed no baffling. However, more refractory elements would require higher temperatures and would evolve more slowly from the boat. Thus the continuum emission would be more intense and probably overlap the desired atomic signal in time. Baffling would alleviate this problem, but a narrower detector bandwidth would also be required.

Our detector consists of an RCA 1P28 photomultiplier mounted at the exit slit of a model 216 McPherson monochromator. This 1-m, f/8 instrument has a reciprocal dispersion of 0.83 nm/mm. With lead we used a slitwidth of 1.5 mm giving a 1.23-nm bandwidth. The lack of background radiation from active nitrogen and the temporal separation of the atomic lead signal from the blackbody emission made this possible. However, when higher temperatures are required, the spectral bandwidth can be narrowed to exclude the continuum emission not blocked by baffling.

We analyzed individual samples consisting of 20-μL aliquots of standard Pb solution diluted in 0.3 N HNO₃ (J. T. Baker Chemical Company Ultrex). Lead content in the samples varied from 20 μg (1000 ppm standard solution) to 1 ng (50 ppb). Thus a factor of 2×10^4 in lead concentration was sampled without any modifications in the apparatus or technique. Figure 2 shows the system response as a function

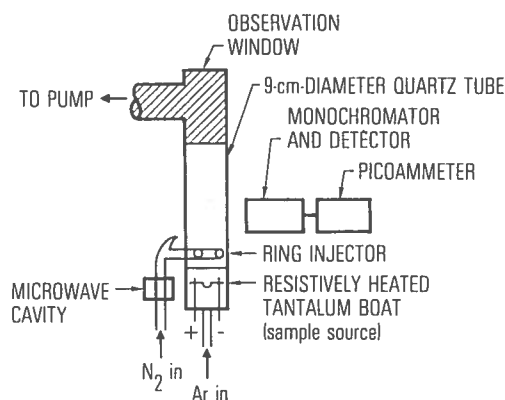


Figure 1. MTES apparatus with sample source adapted for liquid samples

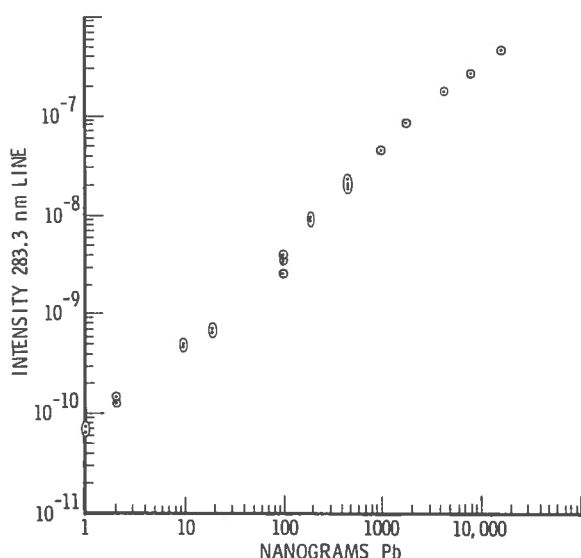


Figure 2. Response of the MTES system to nanograms of lead contained in solution. Note the characteristic flattening of the response curve as saturation is approached

of lead content in the sample.

If one excludes the points obtained with 1, 2, and 20 000 ng of lead, a least-squares fitting procedure on the remaining points yields both a slope and coefficient of determination of 0.99. In other words, the response is linear from 10 to 10 000 ng. Eventually a flattening of the response curve is observed (4, 5) as saturation is approached. The response to samples containing less than 10 ng of lead deviates in the positive direction from linearity. We believe this is due to background interference from the 285.8-nm band of the NO γ -system. This background is currently limiting our sensitivity although dark current fluctuations become significant in comparison to signal with samples containing less than 0.5 ng lead.

Care must be taken to keep the system as leak tight as possible since NO γ -system fluorescence is produced by the reaction of atmospheric oxygen and water vapor with active nitrogen. Should this become a problem, however, ancillary Pb lines at 280.2 and 405.8 nm are suitable for lead detection by MTES.

Recent data from a redesigned apparatus have extended our range in both directions. The new system differs mainly in having a 4-cm diameter quartz viewing tube (Figure 1) with the ring injector built into the wall. Operating at a higher pressure of 4.2 Torr, this design concentrates the sample fluorescence, provides some light baffling, and does not mask or block the effusion of lead vapor from the boat. With this modification, our system response to lead content in the sample is linear from 1.0 to 20 000 ng. A least-squares fit to our new data over this range gives a slope of 0.96 with a coefficient of determination of 1.0. Our minimum detection limit is 0.2 ng (20 μ L of 10 ppb solution). The measurement precision is also improving. Ten successive determinations of a solution containing 10 ppm lead were found to have a standard deviation equal to 10% of the mean value.

In order to test our system on a "real" sample, it was decided to look at the accumulation of lead emitted from automobiles. Five leaves of similar size and shape weighing 4.8 g were taken from a eucalyptus tree adjacent to the San Diego Freeway near the Aerospace Corporation. These leaves were washed with 5.0 mL of the same 0.3 N HNO₃ solution used for diluting the 1000 ppm standard. By the method of standard additions, the concentration of lead in the washing solution was determined to be 22 ppm using the 283.3-nm line. The 405.8-nm line was also used to verify the signal profile. Thus the average 1-g leaf carries on its surface the equivalent of 23 μ g of lead. This is particularly interesting since there had been a rainstorm only three days prior to our collection of the leaves.

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