ANALYSIS OF LEAD IN CANDLE PARTICULATE EMISSIONS BY XRF USING UNIQUANT® 4

Shirley J. Wasson and Zhishi Guo
U.S. EPA, National Risk Management Research Laboratory (NRMRL)
Research Triangle Park, NC 27711

ABSTRACT
As part of an extensive program to study the small combustion sources of indoor fine particulate matter (PM), candles with lead-core wicks were burned in a 46-L glass flow-through chamber. The particulate emissions with aerodynamic diameters <10 μm (PM$_{10}$) were captured on quartz filters and analyzed under vacuum in a Philips PW 2404 wavelength-dispersive X-Ray Fluorescence (WDXRF) Spectrometer. UniQuant® 4 software was used to calculate the filter lead concentrations. Particulate filter loading masses ranged from 0.18 to 52.1 mg. The lead concentrations ranged from 0.2 to 80% by weight, with carbon comprising the remainder of the matrix. The method was validated by analyzing 87 filters, first by XRF and then by EPA Method 12 atomic absorption spectroscopy (AAS). For 84 filters, the average particle mass recovery after XRF analysis was 99 ± 6%. For 84 filters analyzed for lead by both methods, the average recovery of lead by XRF compared to the AAS analysis was 108 ± 9%. Modeling of candle emissions using typical room ventilation scenarios showed that even low-emitting candles can produce a lead concentration above the EPA National Ambient Air Quality Standard (NAAQS) of 1.5 μg/m$^3$ (quarterly average). Burning more than one heavily emitting candle in a poorly ventilated space can produce concentrations exceeding the Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL) concentration of 50 μg/m$^3$ (8-hour time-weighted average).

INTRODUCTION
Since people spend roughly 90% of their time indoors, the level of their exposure to indoor fine particulate matter (PM) has been investigated. Small combustion sources such as unvented heaters, fireplaces, incense, and candles can produce significant indoor PM. When the wick of the candle has a lead core, indoor concentrations and exposure can exceed regulatory lead limits. The lead-core candle wick investigation involved analysis of PM emissions on filters by wavelength dispersive X-ray fluorescence (WDXRF) using a “standardless” method of analysis, UniQuant® 4, and validation of the method by atomic absorption spectroscopy (AAS). The analysis and validation are reported here. The results of the candle study are reported elsewhere (Wasson, 2002).

Atmospheric particulate is routinely collected on Teflon filters and analyzed by energy-dispersive (ED) XRF in a helium atmosphere. (See EPA Compendium Method IO-3.3, 1999.) The instrument used in this study, however, is a Philips PW2404 WDXRF equipped with SuperQ® software for data collection and UniQuant® 4 software (DeJongh, 1997) for data processing. WDXRF generally gives better resolution than EDXRF, but some membrane-type filters, particularly Teflon, generally cannot withstand the vacuum required for the analysis. Although polycarbonate filters perform better than Teflon in vacuum and have little background, they tend to clog easily. For these reasons, the filter was changed to the glass microfiber filters of EPA.
Method 12, and the filter background was subtracted. The resultant count intensities were used in the calculations by UniQuant® 4 to give a concentration for all elements quantifiable by the XRF in percent by weight. To validate the method, we analyzed 87 of the filters by AAS.

METHODS
A total of 100 sets (two or more) of candles was purchased in an estimated 75-mile diameter area centered on Raleigh, NC. Buyers were to select candles with metallic-core wicks or with metallic coverings. The wick was removed from one candle of each set, mounted across a polyethylene liquid sample cup, and secured with a sleeve for qualitative identification by XRF. The excised wick was dissected and the components weighed. An intact candle from each set was then burned in a 46-L glass chamber, 28.6-cm in diameter and 72-cm tall. Air pulled through a high efficiency particulate air (HEPA) filter passed through the mesh bottom of the chamber, around the burning candle, through a glass funnel hood, a PM$_{10}$ cyclone (separates particulate emissions with aerodynamic diameters less than 10 $\mu$m), and a Gelman quartz filter. During the burning period, filters were changed on a regular schedule to prevent overloading with PM. The sequential filters from each test and a filter batch blank were equilibrated in a room climate-controlled to 21.5°C and 34% relative humidity. The loadings were determined to the nearest ±0.005 mg on a six-place Sartorius MC-5 balance, and the diameter measured to the nearest millimeter with a ruler. The filters were then analyzed by a Philips PW 2404 WDXRF using SuperQ® software for collection. Using the loading information, and subtracting the intensity due to the blank quartz filter, the lead concentration was calculated by UniQuant® 4 software in percent by weight. After XRF, the filters were again equilibrated and weighed to determine any loss in the vacuum. The filters were then sent to a commercial laboratory for analysis by AAS using EPA Method 12. The comparison of the WDXRF analysis versus AAS constituted the method validation.

ANALYTICAL CONDITIONS
The Philips PW 2404 XRF instrument is designed with inverted geometry so that the sample is irradiated from below. The loaded quartz filter is placed into a stainless steel sample holder with a 27 mm opening, loaded side down, and secured with an aluminum ring. Each filter is subjected to a full scan to identify all emitted elements. Each of the 111 analyte and 7 background channels is counted for 2 to 4 seconds. For lead analysis a 2.4 kW x-ray beam irradiates the sample. The resulting fluorescence is focused by a 150-$\mu$m beam collimator, resolved by a lithium fluoride (LiF) 220 crystal, and detected by a flow counter. The analysis of each filter requires less than 6 minutes.

UniQuant® 4 was set up at the time of installation to calculate the data collected on the Philips instrument. The setup consists of determining the peak intensities of 65 calibration standards representing 68 measured elements. Another 9 interpolated elements are added for an analysis capability of 77 elements (essentially fluorine through uranium in the periodic table). The sensitivities (“kappas”) in counts per second per mass of each substance in its channel are calculated. The intensity found in the analyte channel due to other elements is also determined and calculated (the line overlaps). The intensities of background positions are determined from the spectra of measured elements which have no intensity at the background position. The analysis consists of determining the concentration of each analyte from its predetermined sensitivity, subtracting the interferences, and subtracting the calculated backgrounds. The analysis
of the sample is reported in percent by weight and the estimated error is given.

Lead mass emission rates (micrograms per hour) were determined for the 16 candles burned. These rates were modeled using a General Purpose Simulation (GPS) model (Guo, 2000a, 2000b) under realistic conditions of ventilation, air circulation, room size, and candle burning scenarios to project possible room concentrations and inhalation by children.

RESULTS
It was found that 50% of the purchased candles had metallic wicks: 33 had zinc wicks (most from the U.S.), 8 had lead wicks (7 from the Far East, 1 unknown), 4 had copper/zinc wicks (all from Mexico), 4 had tin wicks (mixed origin), and 1 had a magnesium wick (“magic” relighting birthday candles). The lead-wick candles were selected for further study. By gravimetry, the wicks ranged from 39 to 74% lead (remainder cotton or other nonmetal), and the linear density of the lead cores ranged from 14 to 27 mg/cm.

The candles were burned until they self-extinguished. From 2 to 13 filters were collected for each candle depending on burning time. A total of 87 filters were analyzed by XRF and compared to AAS. Of the total, 84 agreed well with an average recovery of 108 ± 9%. The recoveries were calculated by the equation

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\%\text{Recovery} = \frac{\text{Lead}_{XRF}}{\text{Lead}_{AAS}} \times 100
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The recoveries are graphically illustrated in Figure 1. The three filters for which XRF varied by a large percentage from AAS were below the detection limit for the XRF (estimated at 0.01 mg lead) and were determined by graphite furnace AAS.

To determine the extent of any filter loading loss during XRF analysis the filters were re-equilibrated and re-weighed. The average loading for the second weighing recovered the loading for the first weighing by 99±6% excluding three outliers. Two of the outliers were due to loss of pieces of the brittle quartz filters upon handling. The other outlier inexplicably gained weight during handling. The gravimetric recoveries are graphically illustrated in Figure 2.

Lead mass emission rates for the 16 candles burned ranged from about 100 to 1700 g/hr. Using a general purpose simulation (GPS) model (Guo, 2000a and 2000b) under realistic conditions of room size, ventilation rate, air exchange with outdoors, and particle deposition velocity, one candle emitting lead at the median rate of 900 g/hr is projected to elevate the source room concentration to 5 times the EPA National Ambient Air Quality Standard (NAAQS) of 1.5 g/m³ in less than 90 minutes. Burning one highest emitting candle is projected to elevate the source room concentration to 11 times the standard in the source room and twice the standard in other rooms in the house in 90 minutes. Burning three candles emitting at 1700 g/hr is
Figure 1. Percent Lead Recovery Distribution, XRF vs. AAS

Figure 2. Percent Loading Recovery Distribution After WDXRF
is projected to achieve the Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL) concentration of 50 \( \text{g/m}^3 \) (8-hour time-weighted average) for lead in the source room in 90 minutes.

The Consumer Product Safety Commission’s (CPSC’s) guideline for a child’s daily intake of lead from consumer products is 15 \( \text{g} \) (16 CFR 1500.230). For several of these candle-burning scenarios, a child not even located in the room with the candles but elsewhere in the house can inhale enough lead to surpass CPSC’s recommended limit in a few hours.

CONCLUSIONS
This project showed that data collection by WDXRF and calculation by UniQuant® 4 software is a valid method to measure lead in a thin layer of carbon particulate on filters. The study of lead-wick candles shows that burning even one such candle can produce hazardous indoor air and dust conditions. Multiple candles can produce substantial lead concentrations even in adjoining rooms where the candles are not burning.

REFERENCES


