

**DEVELOPMENT OF A SENSITIVE REAL-TIME MONITOR FOR  
ELEMENTAL COMPOSITION OF WORKPLACE AEROSOL PARTICLES**

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**ABSTRACT**

The best warning of human exposure to elevated toxic aerosol particles is a monitor that can provide a near-real-time alarm function. Use of surrogate indices such as particle- number concentration, mass concentration, and/or other flow-diagnostics variables is ineffective and could be costly when false positives do arise. We have developed a field- portable system specifically for monitoring beryllium particles in the air in near real-time. The prototype monitor is housed on a two-shelf handcart that can be used in workplaces involving beryllium extraction, machining, and parts fabrication. The measurement involves no sample preparation and generates no analytical waste. The operating principle of the monitor is laser-induced electrical-plasma spectrometry assisted with aerosol-focusing technology. Performance data of the monitor indicates a dynamic range spanning over four orders-of- magnitude, and the monitor is capable of detecting an airborne beryllium concentration of  $0.05 \mu\text{g m}^{-3}$ . In reference, the Department of Energy standard for beryllium is  $0.2 \mu\text{g m}^{-3}$  within an 8-hour average, while the Occupational Safety and Health Administration standard for beryllium is  $2 \mu\text{g m}^{-3}$ . In addition, the monitor is capable of simultaneous detection of multiple elements using an Echelle spectrometer. The capability of simultaneous detection provides a convenient means for positive identification, and possible quantification of multiple elements in near real time. We will present the beryllium results and show applications of the technology to simultaneous detection of several elements embedded in aerosol particles.

**KEYWORDS:** Beryllium, Aerosol Particles, Laser-based measurement, Real-Time Monitor, Aerosol-Beam Focusing

## INTRODUCTION

Beryllium (Symbol: Be; CAS registry ID 7440-4107) is a light element. Beryllium has unique characteristics that make it a superior material for certain specialized applications. Beryllium has a high melting point, a low electrical conductivity, superior strength and stiffness, high thermal conductivity, and high resistance to corrosion. Beryllium is used in several forms: as a pure metal, as beryllium oxide, and as an alloy with copper, aluminum, magnesium, or nickel. Beryllium can be used as X-ray windows (Be transmits X-rays 17 times better than aluminum). A 2% Be alloy with nickel is used for springs, electrodes and non-sparking tools. Beryllium (2%) alloyed with copper gives a hard strong alloy with high resistance to wear used in gyroscopes, computer parts, and instruments (desirable lightness, stiffness). Beryllium alloys are also used as a structural material for high-performance aircraft, missiles, spacecraft (such as the USA space shuttle), and communication satellites. It can be used in ceramics, as a moderator in nuclear reactions since it is a highly effective moderator and reflector for neutrons. Beryllium oxide is extensively used in the nuclear industry.

Beryllium has no known, beneficial biological role. In fact, compounds containing beryllium are poisonous. Beryllium metal dust can cause major lung damage and beryllium salts are very toxic. One route for beryllium into the biosphere is by way of industrial smoke. It is well known that exposure to beryllium particles is associated with chronic beryllium disease, CBD (Sterner and Eisenbud, 1951; Kreiss et al., 1996; Kreiss et al., 1997; Eisenbud, 1998). CBD is prevalent among beryllium metal, oxides, and copper-alloy workers despite significant reductions in total beryllium particle mass exposure (Eisenbud, 1998). Current occupational exposure limit is 2  $\mu\text{g m}^{-3}$  of beryllium per cubic meter of air ( $\mu\text{g m}^{-3}$ ) by the Occupational Safety and Health Administration (OSHA), and is 0.2  $\mu\text{g m}^{-3}$  by the Department of Energy (DOE). Those stringent standards have not prevented new cases of CBD (Eisenbud, 1998), new investigations have been prompted toward hypothesis that the toxicity of beryllium particles that caused CBD may be related to the size of beryllium particles and the surface area of the particles (Stefaniak et al., 2003).

Measurement of beryllium particles in the air has traditionally been performed by a filter-based collection technique followed by Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES). This technique is time consuming, labor intensive, prone to contamination, and possibly does not provide fully useful data with which to protect workers' health. It is likely that workers can be exposed to an elevated level of beryllium particles for a short period; thus, the exposure (dose  $\times$  duration) is still within the OSHA or DOE limit. Such an exposure scenario would not be prevented with the current 8-hr TWA limit. Also, it is likely that workers might be exposed to low-dose of beryllium in ultrafine or nano-beryllium particles that have little beryllium mass concentration. Either scenario calls for a more responsive beryllium monitor for use within the workplace. The research and development efforts taken by DOE at ORNL and Y-12 facilities have produced such a monitor suitable for use as a real-time alarm within beryllium workplaces.

## MATERIALS AND METHOD

The beryllium standard solution was available from the High Purity Standards, Inc. as a 10.5  $\mu\text{g}$  Be/ml in 2%  $\text{HNO}_3$  solution. A 6-jet nebulizer (BGI, Inc.) was used to generate liquid droplets that contain the beryllium salt. The droplets then pass through a diffusion-drying column and enter into a 30-L steel drum to be mixed with the particle-free dilution air. The dried particles follow a lognormal distribution with the geometric mean diameter at approximately 700 nm and the geometric standard deviation close to 2.1. Fig. 1 shows the aerosol-generation setup.

A parallel time-integrated sampling effort was made to collect beryllium particles on TEFLO<sup>®</sup> filters for subsequent laboratory analysis by Inductively Coupled Plasma Mass Spectrometry. The filter analysis was performed by the certified analytical laboratory services at the DOE/Y-12 facility. The beryllium concentrations measured by the real-time monitor are then compared to those measured on the collected filters from the experiment. Subsequent to successful laboratory development and testing, the real-time Be monitor was tested in a beryllium work area at the DOE facility. During this field test, the monitor was located in a Be buffer zone (a separate room) 15-m away from the work area. Simultaneous sampling was made using a TSI single particle aerosol time-of-flight mass spectrometer (Model 3800), and by a filter-sampling technique.

The real-time Be monitor was developed based on a technique developed by Cheng (2003). The original technique utilized a particle-focusing device to concentrate particles for the spectroscopic analysis of elemental composition on particles (see Fig. 2). Interested readers are referred to Cheng (2003) for further detail of the original technique. We briefly describe the improved technique here. The spectroscopic analysis is based on an established principle called laser-induced plasma spectroscopy (LIPS) or laser-induced breakdown spectroscopy. Micro plasma is formed by focusing a high-power laser beam onto the focal point of the particle beam where particles are concentrated.

When the laser plasma is initiated, the dielectric constant of air is reduced facilitating the formation of second plasma in the confined electrical field (see Fig. 2). The time between the formation of the first and a second plasma is only a few nanoseconds. When the plasma cools, the emitted light is retrieved remotely to a spectrometer equipped with an Echelle spectrograph and an intensified charge-coupled device. The light is analyzed for the spectral lines and the attributes associated with the lines. The area under an identified peak is used for quantitative analysis, while the wavelength is used for elemental identification. In the case of beryllium, the doublet Be (II) of 313.1 nm line is used for quantitative determination. The particle-focusing device serves to introduce the aerosol sample to LIPS and to facilitate the formation of the micro plasma.

## RESULTS

### (1) Measurement of Laboratory-Generated Beryllium Concentration

Fig. 3 shows a comparison between the monitoring readings and the filter measurement of beryllium concentration in aerosols. The error bar was estimated using 7 replicated measurements, and found to be in the range of  $\pm 12\%$  to  $\pm 22\%$ . The classical linear regression

showed the two data sets were positively correlated with an  $R^2$  of 0.92. The residual monitor count was found to be approximately 1000, which we judged to be high. Thus, we decided to fit the data by a modified hyperbolic equation. Nonlinear least-square regression was used in the data fitting and the  $R^2$  value improved to a value of 0.96. This nonlinear equation does go through the origin and appeared to fit the data better. It is likely that the instrument response at the concentration range reported here might be explained better with this nonlinear equation. The analytical uncertainty (coefficient of variation) associated with a Be concentration of  $50 \text{ ng m}^{-3}$  (measured by the filter method) was approximately 16%. The analytical uncertainty for blank, particle-free air was approximately 4%. We did not pursue the detection limit for the Be concentration at the present; every data point shown in Fig. 3 has a signal-to-noise ratio greater than 10. The signal is taken at 311.1 nm, while the noise is taken at an off-the-peak wavelength.

## **(2) Beryllium Particle Measurement in a Work Place**

The beryllium in a work place at the DOE/Y-12 facility in Oak Ridge was monitored on December 17, 2003. The monitor was located in a beryllium buffer area outside of the room. A 15-m long tube was used for sampling air into the beryllium monitor. Clean-up activities were conducted on this day; no production-type activities were performed. During static conditions, no beryllium was observed.

Some beryllium oxide materials were moved around within a containment box near the end of the sampling tube. Fig. 4 shows a Be spike immediately after these materials were moved (labeled Run #13), possibly releasing Be-containing aerosols or dusts. A TSI aerosol time-of-flight mass spectrometer also detected Be during this same event (Fig. 5). The TSI instrument also indicated that the BeO particles were approximately 3 microns in size obtained from the time-of-flight data. The TSI instrument (ATOF-MS) is a single particle instrument; while ABF-LIPS measures ensemble average of Be concentration of many particles. No quantitative data about the beryllium concentration were provided by ATOF-MS. This data set was used to corroborate the ABF-LIPS identification only. Other elements were also identified by the ATOF-MS.

Runs #14-16 appear to be recovering from the Be observed within Run #13. Another spike was observed during Run #21 which corresponded to the time in which a beryllium worker (who was in full protective clothing and respirator) wiped off the ends of the sampling tubes prior to moving the sampling tubes to another location. Fig. 6 shows the ATOF-MS identification of Be particles for this event. It was noticed that the Be peak in the ATOF-MS spectra in Fig. 5 was shorter than the Be peak in the Fig. 6; however, the ABF-LIPS Be peak for Run #21 was shorter than that for Run #13. Although ATOF-MS could not quantify, it is assumed that the number of ion counts in Figs 5 and 6 were correct in a relative sense.

The apparent differences between the ATOF-MS and ABF-LIPS peaks can be explained as follows. Workplace aerosol is a polydisperse complex mixture. Two real-time monitors would not see the same particles even they are collocated. The only realistic comparison to be made in a quantitative sense is to use laboratory-generated particles of known properties. Even under that condition, the sample intervals of the two instruments still need to be compatible to yield comparable results. The ATOF-MS spectra in Figs 5 and 6 were from two single particles, and

the ABF-LIPS results shown in Fig. 4 were from many particles. Other particles in the population might give different ATOF-MS spectra. In short, the ATOF-MS data can be used qualitatively in comparison to the ABF-LIPS data. Both instruments did show identifiable spikes in the Be aerosol concentration at the work place providing a positive verification that ABF-LIPS can be used as a sensitive real-time Be monitor.

## DISCUSSION AND CONCLUSION

An instrument has been developed for a DOE/Y-12 facility for real-time monitoring of Be in the air. During the field demonstration, the instrument was located 15-m away from a beryllium work area, and has shown promising results. In the laboratory evaluation during the development, the instrument showed a high sensitivity in detecting Be particles in the air at mass concentration of  $50 \text{ ng m}^{-3}$  in about 3 minutes. Such real-time measurement ability for beryllium particles in the air has not been reported previously in the open literature. With the combination of our patented particle-beam focusing device, laser-induced plasma spectroscopy, and our new patent-pending electrical enhancement, we have achieved an unprecedented sensitivity for beryllium measurement. This ability could be further developed by the commercial sector into a real-time alarm/monitor for protection of the health of beryllium workers. Finally, the technique we reported here is applicable to other metals embedded in aerosol particles and gas phase mercury. Our technique does not distinguish particulate metals from the gas, the technique measures total content of metals in the sample. Thus, our technique can be particularly useful for an environment where distribution in different phases or phase partition of metals may exist.

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## **DISCLAIMERS**

Mention the use of tradenames or companies does not imply the endorsement by the authors nor by their associated organizations.

## Caption of Figures

Fig. 1	Photo of the aerosol generation setup at the Y12 laboratory. The setup was used to provide particles of various Be concentrations during the instrument development.
Fig. 2	Schematic drawing of the electrically enhanced ABF-LIPS technique
Fig. 3	Calibration curves for the electrically enhanced ABF-LIPS
Fig. 4	Time sequence of ABF-LIPS observations at the Y12 work place
Fig. 5	ATOF-MS mass spectra obtained from a 3.0 $\mu\text{m}$ particle containing BeO and LiH detected at the run of #13 time slot on the ABF-LIPS monitor
Fig. 6	ATOF-MS mass spectra obtained from a 2.5 $\mu\text{m}$ particle containing BeO and LiH detected at the run of #21 time slot on the ABF-LIPS monitor



Fig. 1.

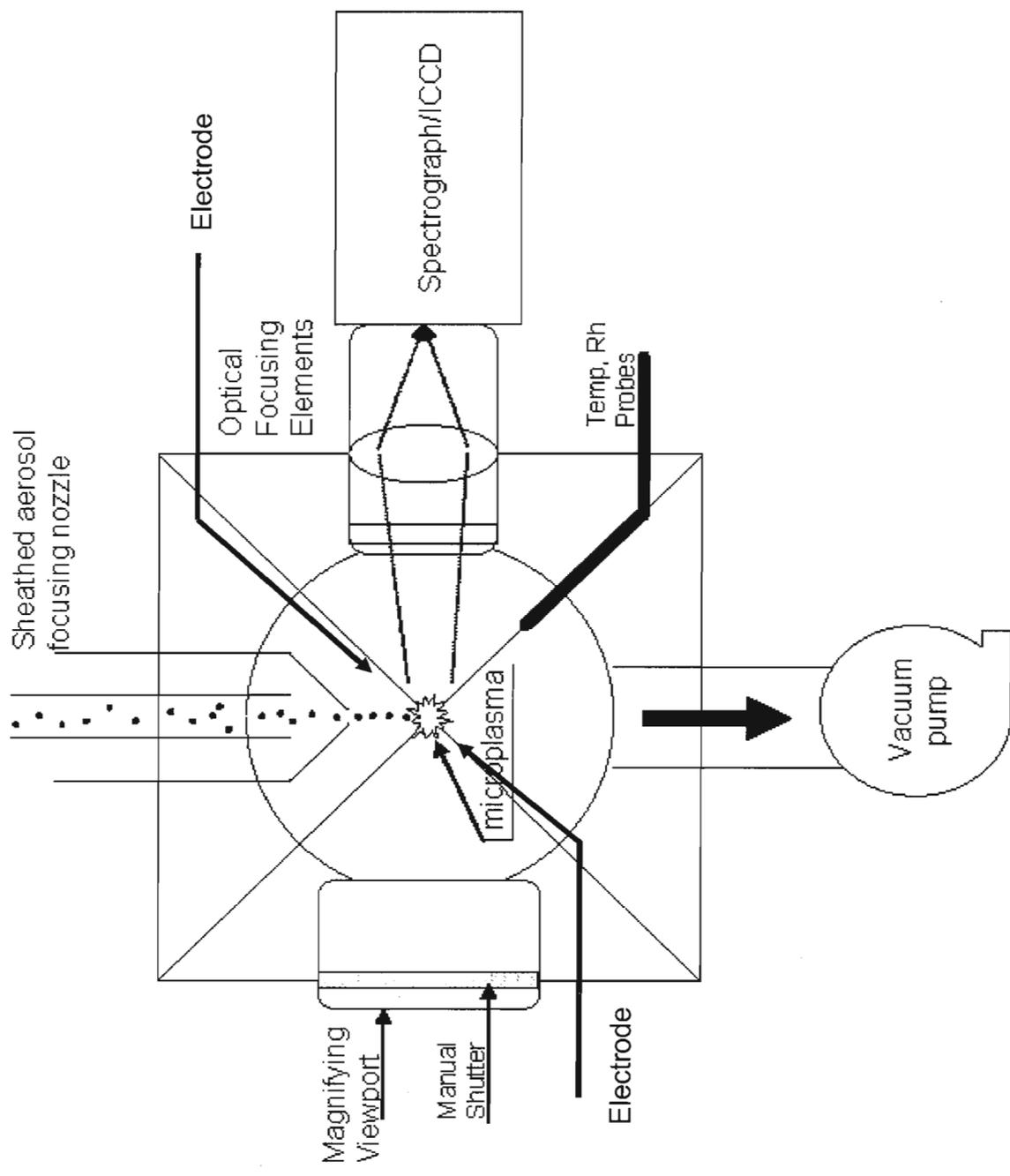


Fig. 2.

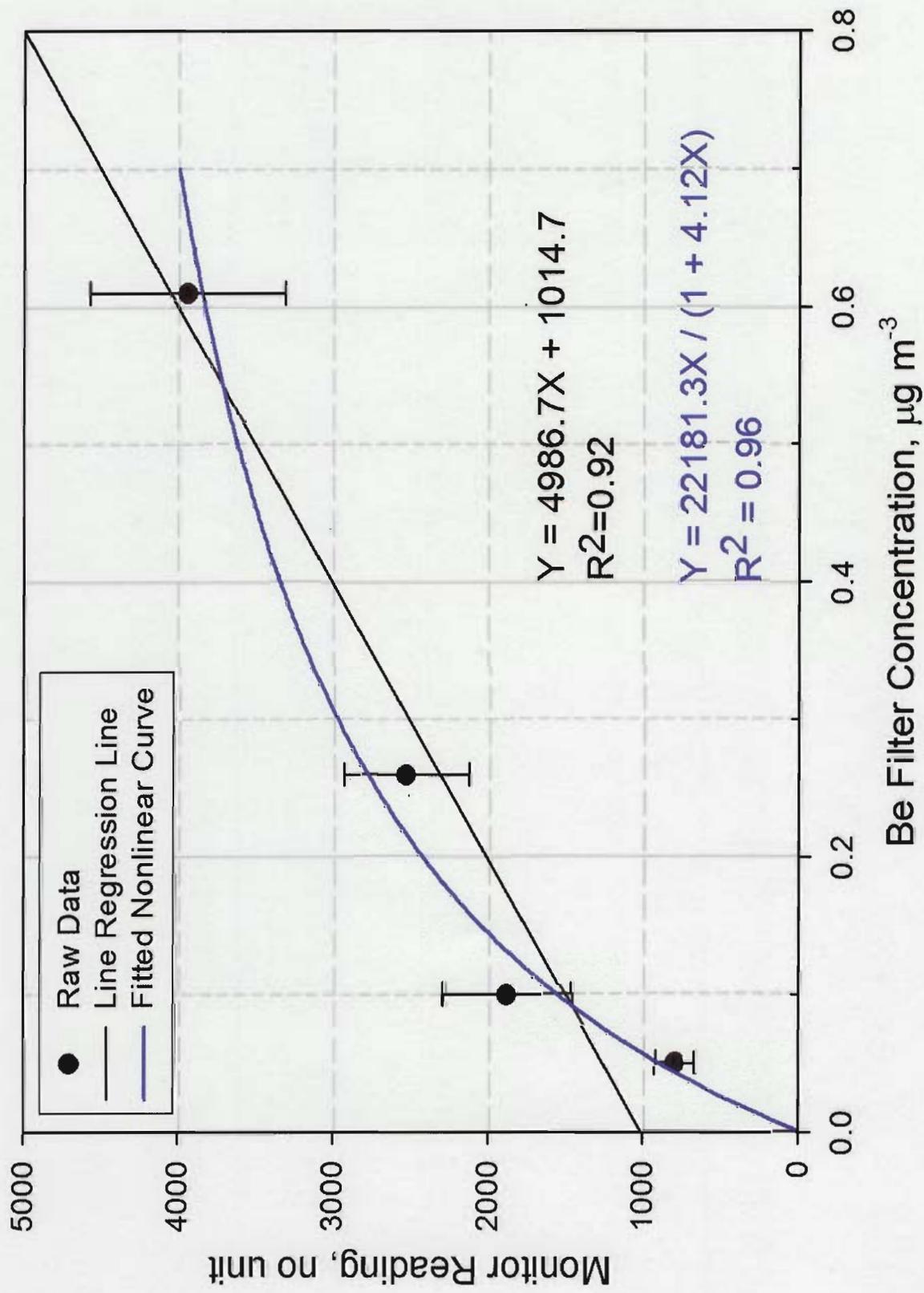


Fig. 3.

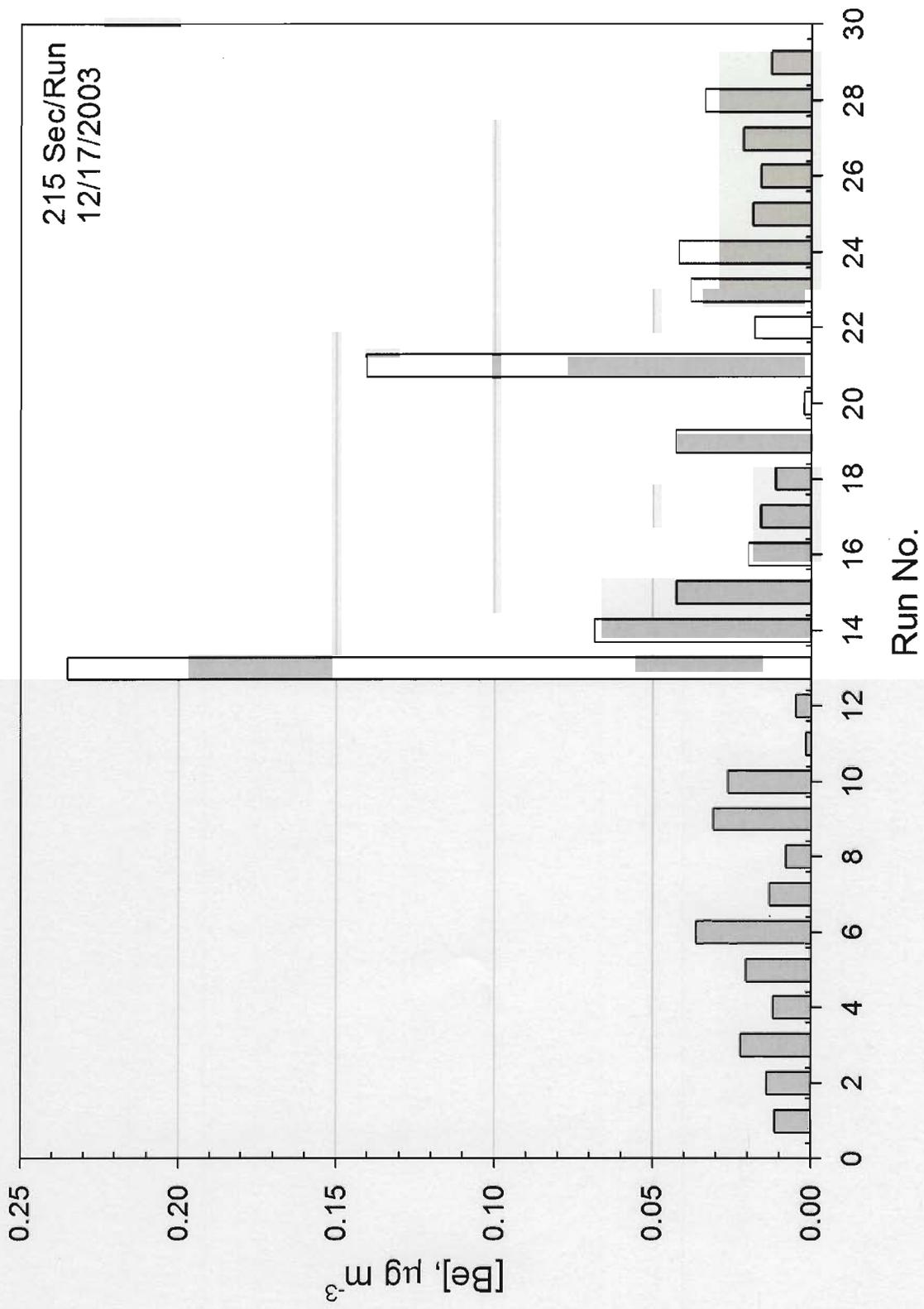


Fig. 4.

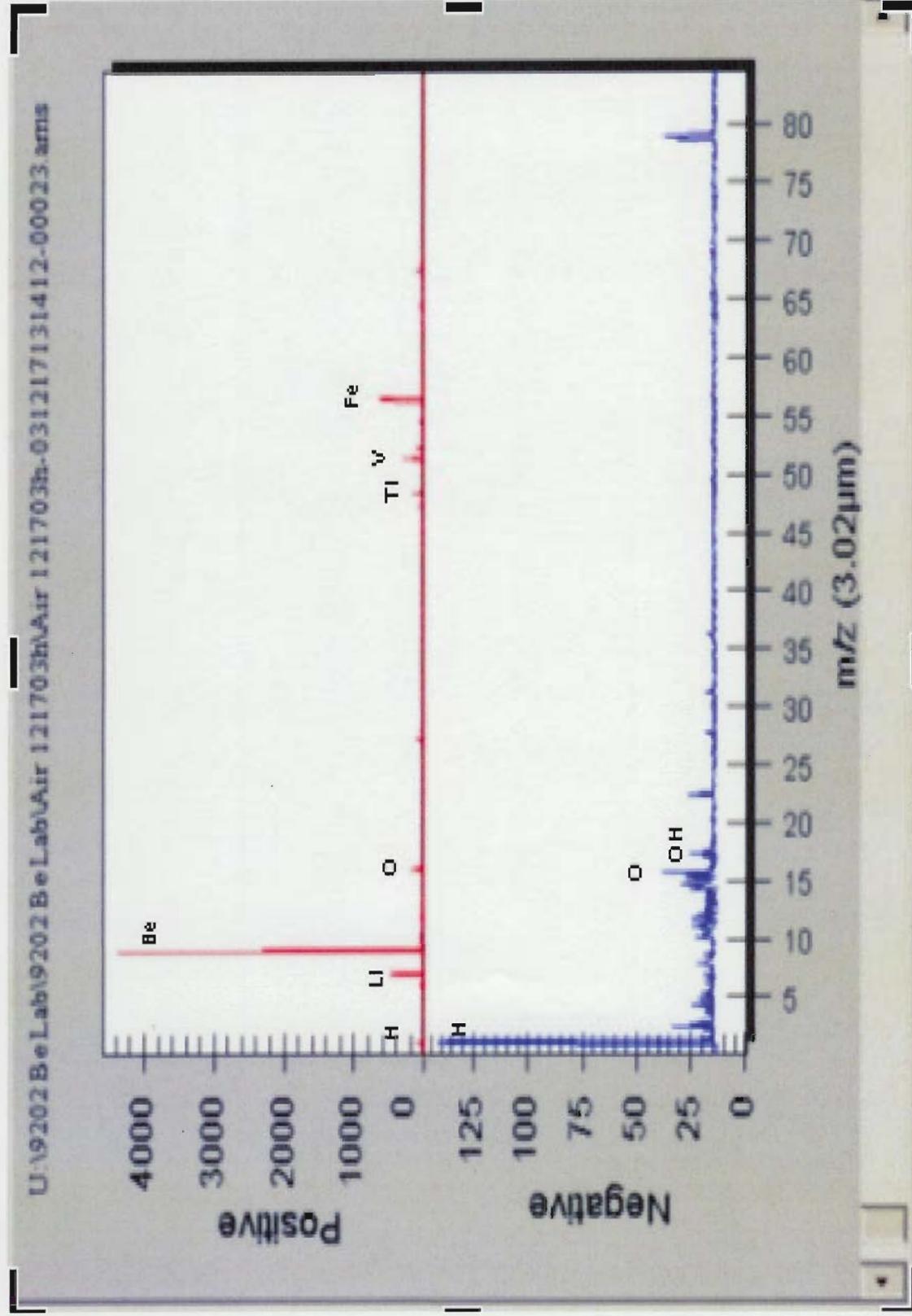


Fig. 5.

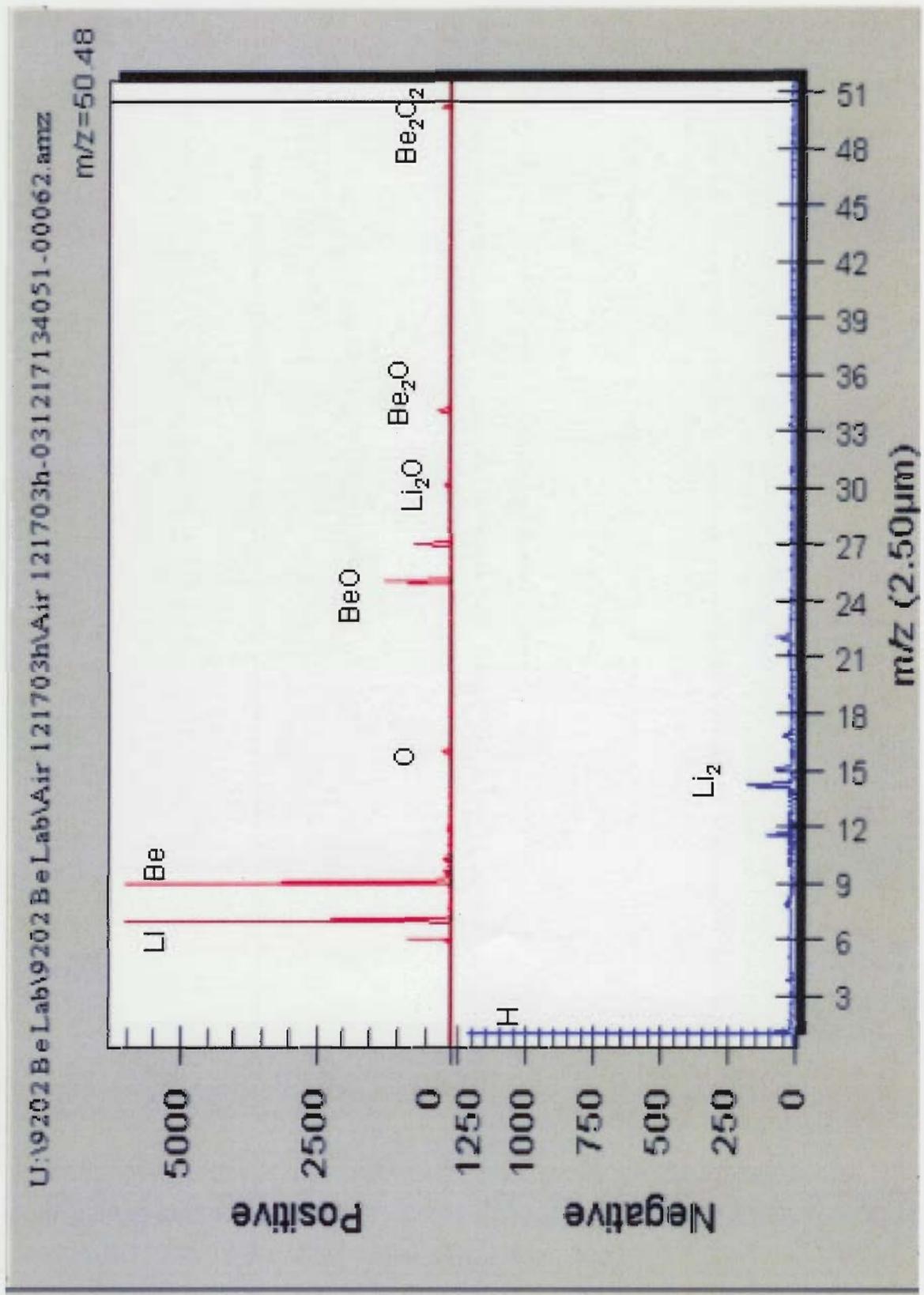


Fig. 6.