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ScienceDirect

Inorganica Chimica Acta 361 (2008) 3069–3074

Inorganica Chimica Acta

www.elsevier.com/locate/ica

Nitric acid dissolution of large mixed cellulose ester filters for beryllium determination

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Received 8 October 2007; received in revised form 29 January 2008; accepted 31 January 2008
Available online 7 February 2008

Dedicated to Robert J. Angelici

Abstract

Defense program use of beryllium has resulted in the need for a wide variety of sampling methods to assess the potential for airborne beryllium particulates. One technique employed in field sampling uses large (8 × 10 in.) mixed cellulose ester (MCE) filters in high volume air samplers. Standard methods for the acid digestion and analysis of the large MCE filters cannot be utilized as the increase in filter mass leads to an uncontrolled exothermic reaction (open flames). As this compromises data quality and presents a significant safety hazard, we propose here an alternative method for digesting these large filters to ensure a solution compatible with ICP-AES (inductively coupled plasma-atomic emission spectroscopy) analysis. The method is a modification of well accepted hot plate digestion methods, which avoids the use of the most hazardous acids such as perchloric or hydrofluoric. While only beryllium was investigated, it is likely that other metals on filters could be digested by this method. Filter media were spiked with a variety of beryllium sources to test the digestion, including beryllium solution spikes, beryllium metal, beryllium oxide and beryllium in soil. Recovery of beryllium metal (103%), beryllium in soil (96%) and beryllium solution spikes (93%) were excellent.
Published by Elsevier B.V.

Keywords: Beryllium; Air sampling; Analytical; Dissolution; Laboratory safety

1. Introduction

Beryllium (Be) is an important and valuable element in aerospace and defense applications due to properties including low mass, high strength and melting point, good electrical conductivity and resistance to corrosion [1]. Unfortunately, occupational exposure to beryllium may lead to the development of chronic beryllium disease (CBD) in some individuals [2–4], an incurable, progressive lung disease. Consequently, the Occupational Safety and Heath Association (OSHA) has set a permissible exposure limit of 2 μg/m^3 (8 h time weighted average or TWA) for allowable airborne beryllium levels in the industrial workplace. The incidence of chronic beryllium disease in workers and former workers within the DOE complex [5–7] led to the establishment of the Chronic Beryllium Disease Prevention Program which sets an even lower action limit of 0.2 μg/m^3 for Department of Energy (DOE) workers [8]. In 2005, the American Conference of Governmental Industrial Hygienists (ACGIH) proposed to lower the beryllium thresholds for the 8 h TWA and the short-term exposure limit to 0.05 and 0.2 μg/m^3, respectively [9].

Beryllium operations have been conducted at Los Alamos National Laboratory (LANL), since the 1940s, and a retroactive summary of beryllium use and assessment of historical exposure was recently published [10]. Beryllium use continues in a number of defense related applications at LANL, including open-air explosive testing. Since it cannot be replaced in these experiments, beryllium use in these tests is carefully controlled and monitored.

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0020-1693/$ - see front matter Published by Elsevier B.V.
doi:10.1016/j.ica.2008.01.039

The goals of the monitoring program are to assess the dispersal of Be in the environment and to monitor its movement during explosive experimentation. This has been accomplished through the use of standard industrial hygiene surface wipe samples to determine residual surface contamination at a site after an experiment, as well as soil sampling to characterize the outdoor firing sites. These methods are useful for characterizing a site after an experiment is complete, but do not provide an accurate picture of what occurs *during* an explosive experiment. Air sampling is one method to measure the dispersal of airborne beryllium.

Sampling methods have been established by OSHA, NIOSH (National Institute of Safety and Health), and other agencies for measuring exposure of workers to various airborne particulate hazards [11–13]. These techniques are designed to measure an individual's exposure to a particular hazard by sampling from the breathing zone; sampling volumes, designed to mimic the intake of air by the worker, are small relative to the volume of an explosive plume. Data from personal air sampling therefore cannot be accurately used to assess release from short-lived explosive experiments. High-volume air samplers ($\geqslant$40 cfm) are being used to sample large volumes of air close to the detonation site, therefore providing more meaningful data about airborne releases from an explosive experiment.

In this study, various filter media were investigated for their suitability as substrates for sampling high volumes of air during explosive experiments. Suitability was judged based upon the ease and effectiveness of filter matrix dissolution, to ensure that entrained particles would be accessible in the digestion, as well as the purity of the matrix. Once a matrix was selected, multiple dissolution methodologies were explored to determine an effective and safe means for dissolving the media and trapped particulates.

Many different filter types were considered for environmental air sampling including glass fiber, PVC, polypropylene and mixed cellulose ester (MCE). Quartz and glass fiber filters presented a problem in that they contain trace beryllium, uranium, lead, and other metals that result in an unacceptable background for analysis [14,15]. Although PVC, PTFE, or polypropylene filters are used for collection of high-volume air samples, we found that for trace beryllium analysis these matrices were difficult to fully digest or that the use of perchloric or hydrofluoric acid was required [11,12,16]. Microwave digestion of polypropylene filters was recently demonstrated but only on small (not high volume) air filters [17]. In the interest of maintaining a simple and milder digestion, the mixed cellulose ester filters were selected for further testing.

MCE filters for high-volume applications were also appealing as OSHA [11] and NIOSH [12] both specify this media for personal air sampling and because dissolution of the filter media can be accomplished with relatively mild acids and reagents. MCE filters are also available in known pore sizes. One report has found MCE filters to be the most suitable in high-volume/high-velocity sampling applications similar to the type we are targeting [18]. One consideration of MCE filters is that they are relatively brittle, a concern that is increased due to the large size of the high-volume air filters. Sampled particles that are not well-entrained into the filter matrix could be easily lost during handling. Thus we did not pursue subdivision of the filters as an option in this investigation, even though subdivision is allowed for certain certified methods.

Previously described dissolution methods for MCE [11,12], when scaled up for the dissolution of standard high-volume environmental air filters (20.3 × 25.4 cm or 8 × 10 in. rectangular filters), caused the filter medium to combust. Since open flame events not only lead to loss of analyte but also present a real safety hazard, we researched alternative methods for the dissolution of these large filters. We propose a modified hot plate method for the preparation of these samples for beryllium analysis by ICP-AES (inductively coupled plasma-atomic emission spectroscopy). The proposed method is mild and effective for the dissolution of MCE filters used in high-volume air sampling. A series of MCE filters were digested using nitric acid on a hot plate, and recovery of beryllium from a standard spike solution, a certified soil, and beryllium metal were shown to be excellent. This simple dissolution results in a solution with low background appropriate for ICP-AES analysis.

2. Materials and methods

2.1. Safety considerations

Beryllium metal and beryllium oxide powders are extremely hazardous and are potential carcinogens, with serious consequences from exposure through inhalation, including CBD. All procedures that involve weighing and working with dry powders were performed in a HEPA filtered (high efficiency particulate air filtered) glove box. Additionally, the work environment was carefully monitored for any potential beryllium contamination using both surface swipes and air sampling. While the digestion may be safely conducted in a standard chemical fume hood, any attempts at replicating the oxide spiking portion of this procedure or using dry beryllium powders should be performed by experienced personnel in a glove box and with the guidance of a qualified industrial hygienist.

2.2. Apparatus

2.2.1. Air samplers

Environmental high-volume air samplers from Hi-Q Environmental Products Company (Model HVP-3300BRL) were used to collect background and experimental samples. Samplers have a frame designed to hold an 8 × 10 in. (20.3 × 25.4 cm) rectangular filter over a wire mesh support.