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Determination of beryllium concentrations in UK ambient air

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HIGHLIGHTS

- Ambient UK air filter samples were analysed by ICP-MS for beryllium content.
- The samples were provided by the UK Heavy Metals Monitoring Network.
- Measured beryllium concentrations were significantly below the guidance threshold.
- Current atmospheric beryllium emissions may be overestimated.
- Future monitoring could target specific sources of beryllium emissions.

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ABSTRACT

Air quality monitoring of ambient air is essential to minimise the exposure of the general population to toxic substances such as heavy metals, and thus the health risks associated with them. In the UK, ambient air is already monitored under the UK Heavy Metals Monitoring Network for a number of heavy metals, including nickel (Ni), arsenic (As), cadmium (Cd) and lead (Pb) to ensure compliance with legislative limits. However, the UK Expert Panel on Air Quality Standards (EPAQS) has highlighted a need to limit concentrations of beryllium (Be) in air, which is not currently monitored, because of its toxicity. The aim of this work was to analyse airborne particulate matter (PM) sampled onto filter papers from the UK Heavy Metals Monitoring Network for quantitative, trace level beryllium determination and compare the results to the guideline concentration specified by EPAQS. Samples were prepared by microwave acid digestion in a matrix of 2% sulphuric acid and 14% nitric acid, verified by the use of Certified Reference Materials (CRMs). The digested samples were then analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The filters from the UK Heavy Metals Monitoring Network were tested using this procedure and the average beryllium concentration across the network for the duration of the study period was 7.87 pg m^{-3}. The highest site average concentration was 32.0 pg m^{-3} at Scunthorpe Low Santon, which is significantly lower than levels that are thought to cause harm. However the highest levels were observed at sites monitoring industrial point sources, indicating that beryllium is being used and emitted, albeit at very low levels, from these point sources. Comparison with other metals concentrations and data from the UK National Atmospheric Emissions Inventory suggests that current emissions of beryllium may be significantly overestimated.

1. Introduction

Air quality is an area of increasing global concern, as emissions of pollutants, including heavy metals, from anthropogenic sources such as the combustion of fossil fuels for power generation and transport, or processes such as smelting or mining, continue to rise and public awareness of potential health effects improves. Studies conducted by the World Health Organisation (WHO) show the harmful effects of heavy metals exposure to human health (WHO, 2006; 2012). These typically include, among others, increased risk of cancer and neurotoxic diseases (WHO, 1980; 1993).

In Europe, a whole raft of legislation has been adopted in order to minimise population exposure to airborne pollutants such as heavy metals (European Commission (EC), 2015). European air quality directives require member states to establish and maintain a system for monitoring concentrations of heavy metals and other

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pollutants in ambient outdoor air (EC, 2015). The Air Quality Directive 2008/50/EC (EC, 2008) specifies a target value for ambient concentrations of lead and the Fourth Daughter Directive 2004/107/EC (EC, 2005a) specifies limit values for nickel, arsenic and cadmium. In the UK this monitoring requirement is met by the UK Heavy Metals Air Quality Monitoring Network, operated by the National Physical Laboratory (NPL) on behalf of the Department for the Environment, Food and Rural Affairs (Defra), and from 2016 Defra and the Environment Agency (EA). The network consists of samplers located at 25 different sites around the UK that pump ambient air through cellulose acetate filters and collect the particulate matter (PM_{10} size fraction). The filters are then sent to the laboratory at NPL, prepared by microwave digestion in acid, then analysed for heavy metals by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) (Goddard et al., 2015).

Beryllium is not one of the metals currently monitored by the UK Heavy Metals Network because there is no existing legislative requirement for it in ambient air. However, the Expert Panel on Air Quality Standards (EPAQS) produced a report for the Department for Environment, Food and Rural Affairs (Defra) (EPAQs, 2008), the purpose of which was to provide guideline levels of priority pollutants, including beryllium, in ambient air 'at which no or minimal effects on human health are likely to occur'. Beryllium poisoning has been documented in workers handling all insoluble beryllium-containing materials. Short-term, high concentration exposure can result in acute pneumonitis, whereas chronic beryllium disease (CBD) or 'berylliosis', a form of interstitial lung disease, can arise after long-term exposure. Both conditions can be fatal. The guideline level given for beryllium in the report was 0.2 ng m^{-3} total particulate in the PM_{10} size fraction, as an annual average (EPAQs, 2008).

The main sources of atmospheric airborne beryllium are anthropogenic: refineries, road traffic, domestic and office heating, power stations and waste incinerators (which may be used for the disposal of electrical items e.g. computers and mobile phones that contain beryllium) (EPAQs, 2008). Beryllium is also found in coal, therefore coal-fired power stations and coal slag used as an abrasive in blasting paint will generate airborne beryllium (EPAQs, 2008).

Beryllium is often used in alloys, particularly with copper or nickel, which are used for their high strength and good electrical and thermal conductivities (Beryllium Science and Technology Association, 2016). There are a wide variety of applications for copper-beryllium alloys, including plastic injection and moulding inserts, springs and spring wiring, lightweight structural components for the aerospace and defence industries, non-sparking tools for use in explosive environments, electronic components (relays, switches, connectors), low wear bearings, automotive parts, and telecommunications cables (Materion Corporation, 2015). Nickel-beryllium alloys are used in mechanical and electrical springs that are required to work at high temperatures without deforming. Applications include household oven controls, fire detection equipment, fire suppression sprinkler systems, and in automotive engine and exhaust control systems (Beryllium Science and Technology Association, 2016).

The highest ambient air levels of beryllium have been recorded near factories where beryllium is processed or beryllium-containing products are manufactured (EPAQs, 2008). Eisenbud et al. (1949), found that within 212 m of a beryllium processing plant in Loraine, Ohio, USA, concentrations of beryllium were measured as high as 460 ng m^{-3}, falling to 30 ng m^{-3} a mile (1.61 km) away. In Czechoslovakia, ambient concentrations of up to 17 ng m^{-3} beryllium were measured in a town located near two power plants burning coal with a high beryllium content (Benko et al., 1980).

A study at a roadside location in Birmingham, UK (Harrison et al., 2003) monitored daily concentrations of metals, including beryllium, in various particle size fractions. The mean beryllium concentration found in PM_{10} was 0.05 ng m^{-3}, with individual results ranging from 0.01 to 0.15 ng m^{-3} – approaching the 0.2 ng m^{-3} limit recommended by EPAQs (EPAQs, 2008). To the best of the authors' knowledge, this is the only example of actual measurements of beryllium in UK ambient air to date.

Fig. 1 shows the UK emissions of beryllium from 1970 to 2013. In 1970 the total emissions were 0.043 kilotonnes, the majority of which was attributable to domestic combustion sources. By 2013, road transport was the main contributory source to total emissions of 0.005 kilotonnes (NAEI, 2016).

The aim of this work is to analyse filter samples from the UK Heavy Metals Air Quality Monitoring Network for the concentration of beryllium in PM_{10}, to establish levels across the UK in relation to the EPAQs guideline level of 0.2 ng m^{-3}.

In terms of analytical methodology, microwave assisted digestion using acids provides a fast and efficient preparation technique for environmental samples requiring trace metals analysis that today is considered routine (Sandroni et al., 2003). Heating in closed vessel systems results in an increase in pressure as the digestion acids evaporate and gases are produced by the decomposing sample matter, thus increasing the boiling point of the reagents and aiding the rapid breakdown of the sample matrix (Lamble and Hill, 1998). There are a number of digestion procedures documented for beryllium in workplace air sampled onto filters in the literature (Ashley et al., 2005) (Brisson et al., 2006), and (Oatts et al., 2012) on which the method in this paper was based. Instrumental analysis by ICP-MS is a well-established technique for the determination of ultra-trace levels of metals, including beryllium (Harrison et al., 2003), (Ashley et al., 2005), so was employed in this study to analyse the digested filter samples.

2. Experimental section

2.1. Test samples

Certified reference materials (CRMs) were chosen that most closely resembled the network samples (PM on filters) in terms of sample media. The CRMs measured were NIST SRM 1944, a mixture of marine sediment collected near urban areas in New York and New Jersey purchased from NIST (National Institute of Standards and Technology, USA) and 'Be from BeO on Filter Media', produced by High Purity Standards (HPS), USA, purchased from Greyhound Chromatography. This material consists of mixed cellulose ester filters (37 mm diameter, 0.8 μm pores) spiked with a stock solution prepared from NIST SRM 1877 (beryllium oxide (BeO) powder, prepared from high fired BeO).

The filter samples tested were sourced from the UK Heavy Metals Monitoring Network. The network filter samples consist of PM_{10} from ambient air sampled onto cellulose ester filters (47 mm diameter, 0.8 μm pores, purchased from Pall Corporation). From each monitoring site, three to five months' worth of filters were tested, sampled between March and July 2016. As concentrations of heavy metals in ambient air are not subject to significant seasonal variation (Goddard et al., 2015), concentrations measured over this substantial proportion of the year should yield average concentrations strongly indicative of an annual average.

2.2. Sample preparation

Samples were prepared by microwave acid digestion (Anton Paar Multiwave 3000). Sub-samples of the reference material NIST 1944 were accurately weighed on a calibrated balance (Sartorius LA230S, resolution 0.1 mg). The 'Be from BeO on Filter Media' reference material filters were digested directly as whole filters. The network