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Determination of hexavalent chromium concentration in industrial waste incinerator stack gas by using a modified ion chromatography with post-column derivatization method

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ABSTRACT

An ion chromatography with post-column derivatization with 1,5-diphenylcarbazide (IC-DPC) analytical method was modified to enable measurement of trace-level hexavalent chromium (Cr(VI)) in air. One of the difficulties in determining trace levels of Cr(VI) in air with conventional IC-DPC methods is co-elution of the solvent and ion peaks due to high concentrations of ionic compounds in the extract. However, by using gradient elution rather than isocratic elution we were able to fully resolve the Cr(VI) ion peak from the solvent peak without the need for diluting the extract, which would have reduced the minimum quantifiable level of the method. With this method, we were able to detect Cr(VI) in air at concentrations of 5.3 ng/m^3 (assuming a sampling volume of 1 m^3 and a final solution volume of 10 mL). Recovery tests at three different concentrations of Cr(VI) (50, 250, 1000 ng) were performed with or without fly ash; recovery rates at all the concentrations of Cr(VI), with or without fly ash, ranged from 68% to 110% (mean ± relative standard deviation, 96% ± 11%), and there were no differences in recovery rates with respect to the presence or absence of fly ash. Finally, we used the developed method to determine the concentration of Cr(VI) in stack gases collected from eight industrial waste incinerators located in Japan. The concentration of Cr(VI) in the stack gases ranged from below the method quantification limit to 3100 ng/m^3. The highest concentrations of Cr(VI) detected in the stack gases were two to three orders of magnitude higher than that in ambient air in Japan.

1. Introduction

Chromium exists in the environment primarily in the trivalent and hexavalent oxidation states. Although trivalent chromium (Cr(III)) is a trace element essential for the maintenance of glucose tolerance in the human body, hexavalent chromium (Cr(VI)) is toxic and carcinogenic [1,2]. The United States Environmental Protection Agency (US EPA) and the World Health Organization (WHO) determined the concentration of Cr(VI) in air corresponding to a 10^{-5} risk to be 0.83 and 0.25 ng/m^3, respectively [3,4]. To assess the risks posed by Cr(VI), the atmospheric concentrations of Cr(VI) have been determined by several groups. Borai et al. [5] determined the concentration of Cr(VI) in atmospheric particulate matter collected in Alexandria (Abou Kir, Get-Enab, and El-Max) and Cairo (Tabbin, Ramsis, and Shoubra), Egypt, and reported that although the concentrations of Cr(VI) in atmospheric particulate matter in Abou Kir were below the method quantification limit (MQL), those at the other sites ranged from 6 to 1580 ng/m^3. Nakanishi and Ono [6] reported the concentrations of Cr(VI) in atmospheric particulate matter (suspended particulate matter and PM$_{2.5}$ [particles with a diameter of 2.5 μm or less]) collected in the Japanese prefectures of Tokyo Metropolis, Kanagawa, Osaka, Yamaguchi, and Ehime; the concentration of Cr(VI) in four of the prefectures was below the MQL for suspended particulate matter (MQL, 0.7–1.1 ng/m^3) and

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$PM_{2.5}$ (MQL, 0.5–1.3 ng/m^3), whereas in Kanagawa, the concentration of Cr(VI) was 0.6 ng/m^3 (MQL for $PM_{2.5}$, 0.5 ng/m^3). Li et al. [7] reported concentrations of atmospheric Cr(VI) in residential areas of Sydney, Australia, of less than 0.2 ng/m^3 (reference values, 0.08 and 0.14 ng/m^3) and in industrial areas of less than 0.2 (reference value, 0.09 ng/m^3) to 1.31 ng/m^3. These high concentrations of Cr(VI) compared with the standard values published by US EPA and WHO [3,4], together with the results of previous assessments of the risks associated with exposure to Cr(VI) [8–11], has made exposure to Cr(VI) a serious health concern globally. Indeed, in Japan, Cr(VI) is listed in the *Air Pollution Control Act* as a substance requiring priority action. Despite these previous studies, however, data on atmospheric concentrations of Cr(VI) remain insufficient to precisely determine the real-world risks associated with exposure to Cr(VI) in the environment.

Waste from the leather, paint, electroplating, and textile dyeing industries are suspected to be major sources of Cr(VI) emissions [12]. According to a report published by the Japanese Pollutant Release and Transfer Register, many waste materials containing Cr(VI) are disposed of by means of incineration at industrial waste processing plants, which means that Cr(VI) in the waste materials may be released into the atmosphere via stack gases. Unfortunately, however, information on the amount of Cr(VI) released into the atmosphere via stack gases is limited. Furthermore, although the results of a limited number of studies examining the release of chromium species from municipal waste incinerators are available [13–15], the precise amounts of Cr(VI) released into the atmosphere remain unknown, particularly with regard to the release of Cr(VI) from industrial waste incinerators via stack gases.

One important reason for the lack of available data regarding the concentration of Cr(VI) in the environment and in emissions from suspected pollutant sources is the lack of an appropriate analytical method. Several methods to determine the concentration of atmospheric Cr(VI) have been published [16–19], including standards by the International Organization for Standardization (ISO 16740:2005 *Workplace air—Determination of hexavalent chromium in airborne particulate matter — Method by ion chromatography and spectrophotometric measurement using diphenyl carbazide*; MQL, 40 ng/m^3 [20]) and the United States Occupational Safety and Health Administration (OSHA Method ID-215 (ver. 2) *Hexavalent Chromium In Workplace Atmospheres*; MQL, 3 ng/m^3) in which ion chromatography and post-column derivatization with 1,5-diphenylcarbazide (IC-DPC) methods are used [21,22]. However, these methods have major drawbacks: the ISO method has a high MQL and therefore cannot be used to measure trace levels of Cr(VI), and the OSHA method needs a cumbersome dilution process to avoid exceeding the capacity of the column. To address these issues, Li et al. [7] and Nusko and Heumann [23] developed analytical methods with sufficient MQLs for detecting trace levels of Cr(VI); however, their methods involve inductively coupled plasma mass spectrometry with a dynamic reaction cell and isotope dilution mass spectrometry, which need expensive equipment that is not commonly found in laboratories, and the pretreatment processes are cumbersome. Thus, these previously reported methods are unsuitable as standard means of determining atmospheric concentrations of Cr(VI); a novel means of determining atmospheric concentrations of Cr(VI) is needed. (See Table 1 for a summary of the currently available analytical methods for determining atmospheric concentrations of Cr(VI).)

In the present study, to address the issue of laboratory instrument accessibility, we modified a conventional IC-DPC method to improve its operability and reduce its MQL for the quantification of trace levels of Cr(VI) in air. We then used our analytical method to determine the concentrations of Cr(VI) in stack gases collected from eight waste incinerators located in Japan. This is the first report of the concentrations of Cr(VI) in stack gas released from industrial waste incinerators in Japan.

2. Materials and methods

2.1. Reagents and materials

As a source of Cr(VI), potassium chromate was purchased from Wako Pure Chemical Industries, Ltd., Japan. DPC, potassium hydrogen phosphate (K_2HPO_4), potassium dihydrogen phosphate (KH_2PO_4), magnesium sulfate ($MgSO_4$), sodium carbonate (Na_2CO_3), and sodium hydrogen carbonate ($NaHCO_3$) were also obtained from Wako Pure Chemical Industries, Ltd., Japan. Milli-Q water (Millipore, USA) was used as ultra-pure water. To avoid elution of chromium ions from glassware, all laboratory equipment used was made of polytetrafluoroethylene or perfluoroalkoxy alkane.

2.2. Collection of stack gas samples

In the present study, the choice of filter used to collect fly ash in the stack gas samples was crucial. Cr(VI) is reported to be eluted from quartz filters at 11–21 ng/cm^2 and from polytetrafluoroethylene filters at 1.0–1.5 ng/cm^2 [6]. Nusko and Heumann [23] reported that Cr(VI) was eluted from a glass filter (AP-40; Millipore, USA) at 10 ng/cm^2 [5]. Therefore, in the present study, to minimize the effects of the elution of Cr(VI) from the filters, polytetrafluoroethylene filters (PF020; Advantech, USA) were used. A total of 12 samples of stack gas were collected from eight industrial waste incinerators located in Japan, and fly ash present in the stack gases was collected on the polytetrafluoroethylene filters by using an air sampler. The sampling was carried out for 4 h, and the sampling volume was about 1 m^3.

2.3. Determination of the concentration of Cr(VI)

In the present study, we modified a conventional IC-DPC method to develop an analytical procedure that could be used to determine the concentration of Cr(VI) in stack gases. Fig. 1 shows an overview of the procedure. Under acidic or neutral conditions, or in the presence of ferrous ion, Cr(VI) is reduced to Cr(III) [20]. Therefore, we extracted Cr(VI) from the collected fly ash under basic conditions ($pH > 8$) with $MgSO_4$ to prevent the precipitation of ferrous ion. The filters holding the sampled fly ash were placed in separate 125-mL beakers to which 1 mL of 0.5 M K_2HPO_4/0.5 M KH_2PO_4, 0.5 mL of 10 mg/mL $MgSO_4$, and 5 mL 100 g/L Na_2CO_3/20 g/L $NaHCO_3$ were added. Ultra-pure water was added to the beakers to a total volume of 10 mL, and the solution was heated at 90 °C for 1 h to produce an extract. After heating, the extract was centrifuged, and ultra-pure water was added to a total volume of 10 mL.

The extract after filtration was analyzed by using an ion chromatograph (Dionex ICS-5000+; Thermo Scientific, USA) equipped with an ultraviolet–visible spectroscopic detector and subjected to post-column derivatization with DPC. Potassium hydroxide (KOH) was used as the mobile phase. The Cr(VI)–DPC complex was detected at 530 nm. An IonPac AS20 column (Thermo Scientific, USA) (77.5 μeq/column), which has a 10-fold greater ion-exchange capacity than the IonPac AS17 column (Thermo Scientific, USA) (7.5 μeq/column) that is routinely used for the determination of the concentration of inorganic anions [24], was used under operating conditions for the separation to avoid overloading the column. The metrological parameters of the developed analytical procedure are summarized in Table 2. To compare them with those of OSHA ID-215 (ver. 2), the metrological parameters of OSHA ID-215 (ver. 2) are also shown in Table 2.