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## Emissions of fluorides from welding processes

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### ARTICLE INFO

#### Article history:

Received 8 January 2015

Revised 30 March 2015

Accepted 31 March 2015

Available online 26 June 2015

#### Keywords:

Fluorides

Particle size distribution

Welding processes

### ABSTRACT

The levels of fluoride airborne particulates emitted from welding processes were investigated. They were sampled with the patented IOM Sampler, developed by J. H. Vincent and D. Mark at the Institute of Occupational Medicine (IOM), personal inhalable sampler for simultaneous collection of the inhalable and respirable size fractions. Ion chromatography with conductometric detection was used for quantitative analysis. The efficiency of fluoride extraction from the cellulose filter of the IOM sampler was examined using the standard sample of urban air particle matter SRM-1648a. The best results for extraction were obtained when water and the anionic surfactant *N*-Cetyl-*N,N*-trimethylammonium bromide (CTAB) were used in an ultrasonic bath. The limits of detection and quantification for the whole procedure were 8 µg/L and 24 µg/L, respectively. The linear range of calibration was 0.01–10 mg/L, which corresponds to 0.0001–0.1 mg of fluorides per m<sup>3</sup> in collection of a 20 L air sample. The concentration of fluorides in the respirable fraction of collected air samples was in the range of 0.20–1.82 mg/m<sup>3</sup>, while the inhalable fraction contained 0.23–1.96 mg/m<sup>3</sup> of fluorides during an eight-hour working day in the welding room.

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### Introduction

The impact of fluorides in the environment constantly draws attention. They are emitted in both gaseous and particulate forms into the air by different types of coal-burning and industrial operations, such as power generation and the production/manufacture of aluminum, glass, plastics, steel, fertilizers, and ceramics. Industrial sources of fluoride alter the structure and composition of plant communities and cause fluoride to enter other links of the trophic network (Franzaring et al., 2006). Several studies have been devoted to fluoride deposition on the land surface, accumulation in soil and penetration into groundwater deposits (Mirlean and Roisenberg, 2007; Mishra et al., 2009; Dobaradaran et al., 2009;

Mishra and Damodaran, 2011; Walna et al., 2013; Susheela et al., 2013). In areas subjected to fluoride emissions, adverse effects have been observed in the bone systems of both animals and humans (Weinstein and Davison, 2004; WHO, 2012).

Welding is the principal industrial process used for joining metals. The procedure of welding is simple but its health implications are complex. Welding fumes consist of a wide range of gases and metal fumes, which are generated mostly from the electrode/wire feed. Their chemical compositions depend upon various factors like type of welding, metal coating, material of the electrode and type of metal being welded. Therefore, welders are exposed to a number of complex mixtures of compounds, including fluorides, which

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pose a serious threat to their health. Welding fume pulmonary effects have been associated with bronchitis, cancer and functional changes in the lung (Flynn and Susi, 2010; Chadha and Singh, 2013). It was shown that during several welding processes, significant concentrations of ultrafine particles are emitted and deposited in the lungs of exposed workers (Gomes et al., 2012a, 2012b). The emission of airborne particles increased with current intensity and an exponential decay of nanoparticle density with distance to the weld area was observed. Emitted fluorides have been associated with particulate matter, which is a mixture of suspended particles and aerosols. The size of airborne particles determines the parts of the respiratory tract in which the particles are deposited. The studies by Li et al. (2003) showed that small airborne particles have a high probability of depositing deep in the respiratory tract. Fluorides adsorbed onto the respiratory fraction (which corresponds to particles whose aerodynamic diameter is in the range of 0–100  $\mu\text{m}$ ) of suspended material may penetrate the gas exchange region of the lung, causing damage to the alveolar tissues and inducing various health problems (Brunekreef and Holgate, 2002). Information from different sources indicates that long-term exposure of humans to fluorides at 0.1–0.5  $\text{mg}/\text{m}^3$  concentration level leads to impairment of respiratory function and skeletal fluorosis (Alexeeff et al., 1993).

In view of the increasing importance of small particles in exposure assessment, this study reports the analysis of fluoride airborne particulate levels emitted from welding processes. The IOM (patented IOM Sampler, developed by J. H. Vincent and D. Mark at the Institute of Occupational Medicine (IOM)) personal inhalable sampler was used for collection of air samples. This sampler offers the advantage of being able to sample the inhalable and respirable size fractions simultaneously and closely simulates the manner in which airborne workplace particles are inhaled through the nose and mouth.

## 1. Materials and methods

### 1.1. Collection of samples

Air samples were collected in a separated mechanical workroom where metal rods were being welded for the construction of a fence, during welding by an employee. The workroom, with area of around 10  $\text{m}^2$ , was equipped with local gravimetric ventilation. The first sampling point was located at a distance of 50 cm from the source of welding, in the breathing zone of the worker; the second point was at the back, approximately 1.5 m from the floor and at a distance of 1 m from the source, and the third sampling point was at a height of 2 m from the floor, 2 m to the right of the source.

The inhalable fraction was collected onto a polyurethane foam (PUF) disk in the IOM personal inhalable sampler, while the respirable fraction was collected on a mixed cellulose ester (MCE) membrane filter. The samples were collected with a flow rate of 2 L/min. After collection, the foams and filters were stored at 0°C in an ice chest till they were delivered to the laboratory. Subsequently, filters were refrigerated at 4°C.

### 1.2. Extraction procedure

Deionized water, 2.5 mmol/L N-Cetyl-N-N-N-trimethylammonium bromide (CTAB), 2.5 mmol/L sodium dodecyl sulfate (SDS) and the mixture of 4.5 mmol/L  $\text{NaHCO}_3$  + 1.4 mM  $\text{Na}_2\text{CO}_3$  were tested for extraction of fluorides. 10 mg portions of standard sample of urban air particle matter SRM-1648a (from the National Institute of Standards and Technology, USA, Gaithersburg in the state Maryland) were introduced into the tubes and 10 mL of an appropriate extractant were added. The tubes were put in an ultrasonic bath for 30 min. The extracts were separated from the solid phase by centrifuging at 3000 r/min for 30 min, then filtered through 0.45  $\mu\text{m}$  polytetrafluoroethylene membrane syringe filters and used for ion chromatograph (IC) determination.

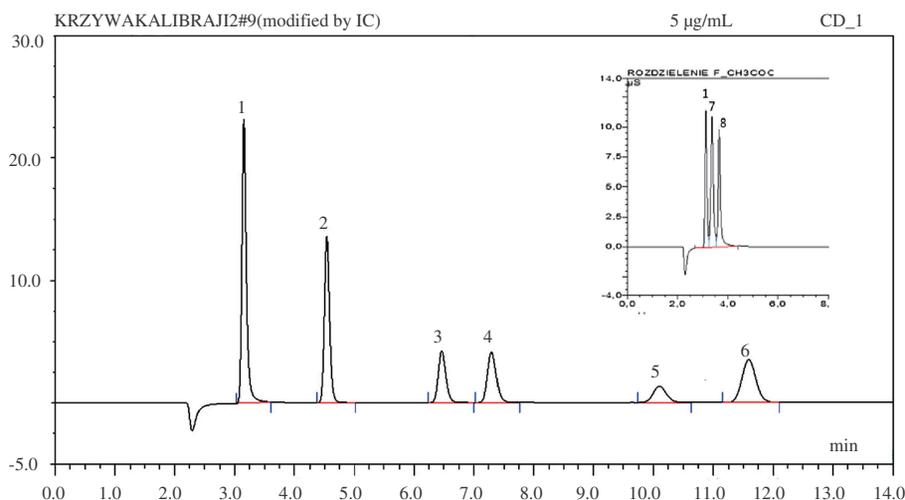
For extraction of fluorides from samples collected in the welding room, the filters and foams were transferred into the corresponding extraction tubes and 10 mL of deionized water was added into the tubes. The other steps for extraction were the same as described above for the SRM-1648a reference material.

### 1.3. Chromatographic analysis

A suppressed-ion chromatograph (Model ICS-500, Thermo Scientific Dionex, USA, Sunnyvale in the state California) was used for the determination of fluorides. The system was equipped with the Dionex IonPac-AS22 analytical column (250 mm  $\times$  4 mm i.d.) and with an IonPAC-AG22 guard column. The ions were detected by suppressed conductivity of the eluent using a conductometric detector. A 50  $\mu\text{L}$  aliquot of each sample/standard was loaded into the eluent stream. The eluent was composed of 4.5 mmol/L  $\text{NaHCO}_3$  and 1.4 mmol/L  $\text{Na}_2\text{CO}_3$ . This eluent composition enables one to achieve baseline separation of inorganic anions and low molecular mass organic acids; particularly, the separation of fluorides from acetate and formate (Fig. 1). The overlapping of these peaks has been reported in the literature (Kontozova-Deutsch et al., 2011). The eluent flow rate was 1.2 mL/min. The column temperature was set at 30°C.

## 2. Results and discussion

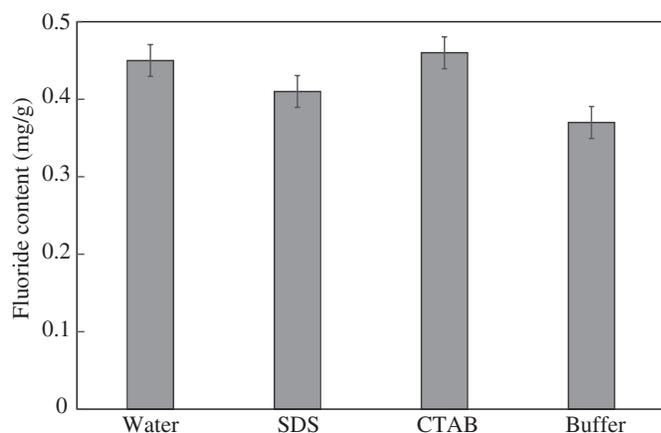
The efficiency of fluoride extraction from the cellulose filter of the IOM sampler was examined using the standard sample of urban air particle matter SRM-1648a. Certified values are restricted to constituent and trace elements and the material certificate also lists complementary concentration values of some inorganic anions including chlorine, nitrate and sulfate. It can be utilized in the evaluation of methods used in inorganic analysis of atmospheric particulate matter and samples with similar matrices (Talebi and Abedi, 2005; Karthikeyan and Balasubramanian, 2006; Karthikeyan et al., 2007; García et al., 2008; Salcedo et al., 2014). Water, two surfactants (cationic CTAB and anionic SDS) as well as a buffer solution ( $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ ) applied for fluoride IC determination were examined. According to Talebi and Abedi (2005), the use of a surfactant in extraction of anions from airborne particulate matter could increase the



**Fig. 1 – Separation of chromatographic peaks of fluoride and inorganic anions from standard solutions on IonPAC AS22 column. Peaks: (1) fluoride; (2) chloride; (3) bromide; (4) nitrate; (5) phosphate; (6) sulfate. Inset: separation of (1) fluoride from (7) acetate and (8) formate.**

extraction yield. The results from these experiments based on at least three replicates are presented in Fig. 2.

The best and most reproducible results for extraction of fluorides were obtained when a water and CTAB solution were used as the solvent. The anionic surfactant SDS and buffer composition gave lower extraction efficiency. These results are contrary to those in an earlier report (García et al., 2008), which showed that the efficiency of extraction of some anions ( $F^-$ ,  $Cl^-$ ,  $SO_4^{2-}$  and  $NO_3^-$ ) from the SRM-1648 material was considerably increased in the presence of CTAB and SDS in comparison to water. Nevertheless, the values obtained in this study for chlorides and nitrates extracted by water from

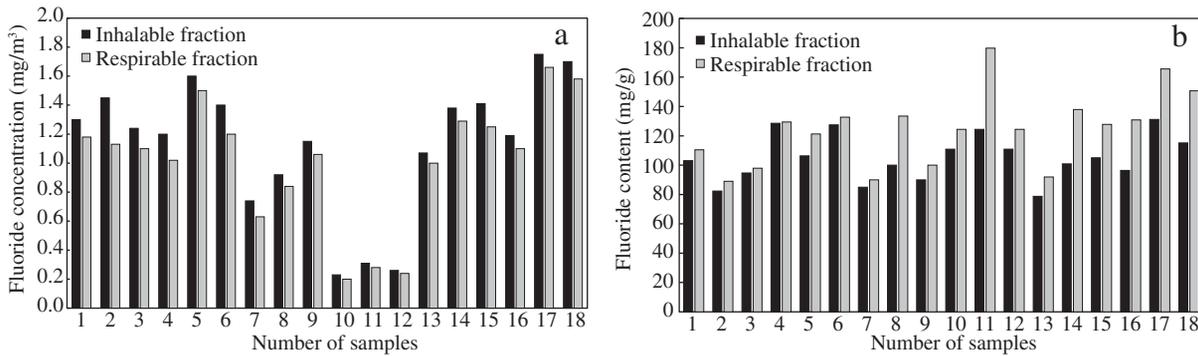


**Fig. 2 – Content of fluorides extracted from standard reference material SRM-1648a collected on mixed cellulose esters (MCEs) filter using water, 2.5 mmol/L sodium dodecyl sulfate SDS, 2.5 mmol/L N-Cetyl-N-N-N-trimethylammonium bromide (CTAB) and buffer (4.5 mmol/L  $NaHCO_3$ /1.4 mmol/L  $Na_2CO_3$ ) solutions. Extraction time: 30 min in ultrasonic bath.**

SRM-1648a are in good agreement with previous reports (Karthikeyan and Balasubramanian, 2006; García et al., 2008). Further, the recovery was determined by processing solutions with known fluoride concentrations in the range of 0.025–5 mg/L using the same experimental procedures. The recovery efficiencies for the analytical procedure ranged from 96% to 102%. Precision (expressed as the coefficient of variation) ranged from 2.1% to 7.9% ( $n = 8$ ).

Procedural blanks were also analyzed concurrently with the samples, however, no detectable fluorides were present. Quantification of fluorides was carried out based on the retention time and peak area of the calibration standards. 10 standards with concentrations in the range of 0.01–10 mg/L (corresponds to 0.0001–0.1 mg of fluorides per  $m^3$  in collection of a 20 L air sample) were used in the analysis calibration. The correlation coefficient of the calibration curve was 0.9994. The limit of detection for the whole procedure, defined as three times the signal/noise ratio ( $S/N$ ), was 8  $\mu g/L$  and the limit of quantification (at  $S/N = 10$ ) was 24  $\mu g/L$ .

After optimization of the extraction conditions, the concentrations of fluorides in the inhalable and the respirable size fractions in air samples collected in welding room were determined. The extraction was carried out with 10 mL deionized water in an ultrasonic bath. During the welding process the concentration of fluorides in the respirable fraction of the collected air samples was in the range of 0.20–1.82  $mg/m^3$ , while the inhalable fraction contained 0.23–1.96  $mg/m^3$  of fluorides during an eight-hour working day. The welding work was not a continuous process; it was performed for 2 hr, then the components were installed and finally welding was continued for another 2 hr (Fig. 3a). There was not a strict correlation between the content of fluorides and the place of sample collection. Regardless of the sampling site, fluorides in the respirable fraction formed a large part (about 80%) of the anion content determined in the inhalable fraction.



**Fig. 3 – Concentration of fluoride in inhalable and respirable fractions (a) based on the volume of air, (b) based on the weight particle, collected at three different locations in the welding room during 6 working hours.**

Application of the IOM Personal Inhalable Sampler offers the possibility of simultaneously examining the masses of the collected fractions. The MCE filters and polyurethane foams were first conditioned in a desiccator for 24 hr and accurately weighed using a microbalance. They were weighed again after collection of the samples. Fluoride contents were in the range of 73.3–179.8 mg/g in the respirable fractions (adsorbed onto the MCE filter) and 72.2–128.5 mg/g in the inhalable fractions (adsorbed onto MCE filter and PUF) (Fig. 3b). It follows that fluorides demonstrate significant ability for adsorption onto the small particles of the respirable fraction with aerodynamic diameter less than 10  $\mu\text{m}$ . They are deposited in the gas exchange region of the lung, and pose serious occupational risk.

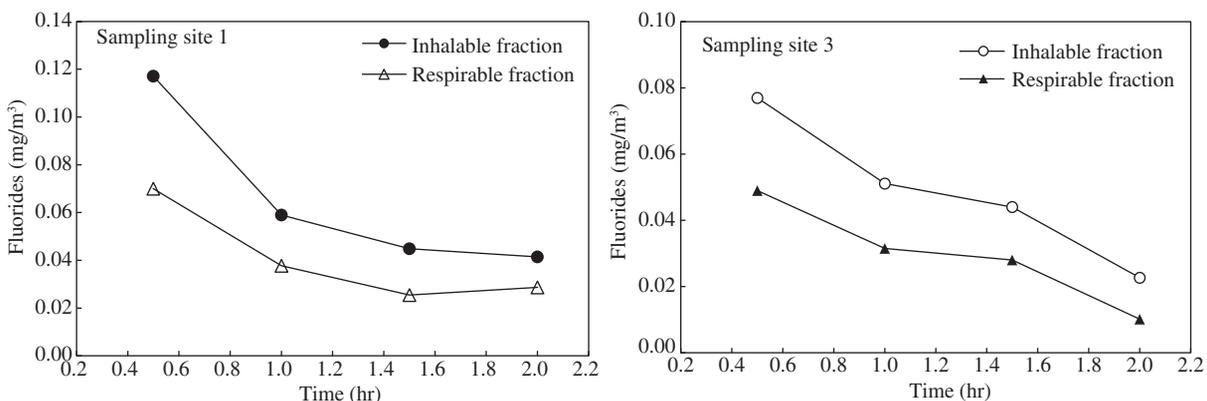
The distribution of fluorides in the studied fractions was also examined depending on exposure time and the sedimentation rate of aerosol. IOM samplers were located in different places in the workroom and the welding processes were carried out only for 10 min. The samples were collected at intervals of 30 min to 2 hr. The changes in the fluoride concentrations at sampling sites 1 and 3 are presented in Fig. 4. The highest concentrations of fluorides were detected at sampling site 1; 0.12 mg/m<sup>3</sup> in the inhalable fraction and 0.07 mg/m<sup>3</sup> in the respirable fraction, respectively. After 2 hr they were decreased by 70% and 59%, respectively, in these

fractions. At sampling site 3, furthest away from the source, fluoride concentrations were 0.08 mg/m<sup>3</sup> and 0.05 mg/m<sup>3</sup> in the inhalable and respirable fractions, respectively. The content of fluorides were decreased by 75%–80% after 2 hr, however, they were still are present in both fractions.

### 3. Conclusions

Welding generates enormous amounts of gases and metal fumes. Their compositions and content depend upon various factors like type of welding, metal coating, material of the electrode and type of metal being welded as well as on intensity of the process, circulation of air, and ventilation. Thus, the welders are exposed to a number of complex mixtures of compounds that pose a serious threat to their health.

The results of the current study indicated that fluorides are a part of the emitted small particles, which can penetrate the human respiratory tract down to the gas exchange regions. This might suggest that the concentration of fluorides should be taken into account while establishing the maximum limit values. Workers exposed to these compounds should be equipped with the appropriate personal protective equipment preventing the infiltration of small particles into the respiratory tract.



**Fig. 4 – Concentrations of fluorides in inhalable and respirable fractions air samples depending on exposure time.**

## Acknowledgments

This work was supported by the Polish Ministry of Science and Higher Education under grant for statutory I-43.

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