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Visualisation and identification of peak exposure events in aluminium smelter pot rooms using hydrogen fluoride and aerosol real-time portable spectrometers

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A recently developed novel portable real-time hydrogen fluoride spectrometer was used with an aerosol PM₁₀ spectrometer under a PIMEX telemetric measurement strategy to visualize and identify simultaneous occupational air peak exposure events to hydrogen fluoride and PM₁₀ aerosol sub-fractions in aluminium smelter pot rooms using Søderberg or Prebake anode technologies. The hydrogen fluoride and the aerosol concentration data measured during different work operations are plotted and evaluated applying the synchronised videos and air concentrations measured by the spectrometers. The main point-emission sources of HF and PM₁₀ were identified and assessed. The major finding in the study was that the main source of PM₁₀ and HF was partly open cells in a Søderberg pot room, whereas in a Prebake pot room, the point emissions of the two contaminants were associated with hot bath residues and hot replaced anodes. In order to prevent the simultaneous exposure to HF and PM₁₀ among pot room workers it is important to prevent workers from being close to these point-sources under unfavourable ventilation. Storage of hot residues outside electrolytic cells without any point source ventilation should not occur.

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Environmental impact

Identification of peak exposure events is essential in order to reduce occupational exposure of workers. This paper describes the use of a novel portable hydrogen fluoride spectrometer used in the primary aluminium industry, in combination with an aerosol spectrometer for identification and explanation of hydrogen fluoride and PM₁₀ peak exposure events. The spectrometers were used in combination with picture mixed exposure (PIMEX) equipment. The results show that the portable spectrometers and the PIMEX methodology are applicable in this industry, despite the presence of strong magnetic fields. This approach has provided the aluminium industry with a tool for peak exposure identification and making cost effective interventions to reduce occupational exposures to hydrogen fluoride and PM₁₀.

Introduction

The fluorides which are evolved from Hall–Héroult electrolytic cells in the primary production of aluminium metal and which contaminate the workroom atmosphere are either gaseous or particulate. The gaseous fluorides generated in the process are mainly hydrogen fluoride (HF), tetrafluoromethane (CF₄), hexafluoroethane (C₂F₆) and silicon tetrafluoride (SiF₄), the major component being HF, which is formed by the reaction of

electrolyte components with adsorbed or crystalline water in raw materials or other sources of hydrogen from the anodes.¹ The particulates are mainly condensation and hydrolysis products from vaporisation of the electrolyte.¹ In recent studies the existence of elevated number concentrations of ultrafine particles formed by condensation both in Søderberg and Prebake pot rooms was shown. The main source of this particle size fraction is evaporation of fluorides from open electrolyte surfaces of the pots.^{2,3} At high relative humidity, comparable with the human respiratory tract, most particles encountered in the Søderberg and Prebake pot rooms either undergo partial deliquescence (leading to a water droplet with an insoluble core) or form a thin water film at the surface. As gaseous HF is highly soluble in water, the aerosol particles may act as carriers for this gas into the alveolar region of the lower respiratory tract. Based on a one-dimensional mass balance model, it was estimated that under *peak exposure* conditions approximately 10%

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of the initial gaseous HF may be transferred to the particle phase. These results indicate that HF may penetrate deeper into the lung in the presence of soluble particles or particles that form surface water films as compared to HF alone.⁴ Thus, in order to prevent workers from experiencing events with simultaneous peak exposure to both HF and hygroscopic aerosols, it is of paramount importance to develop instrumentation and measurement strategies to visualize and identify such events.

There are several detection principles which have been applied in the real-time determination of HF in air. Semiconductor sensors have been developed for measurement of HF, but these sensors suffer from selectivity problems. Metal-insulator-semiconductor structure gas sensors based on silicon or silicon carbide can be applied for the determination of HF, fluorine and fluorocarbons.⁵ If selectivity among these gases is required, three sensors operated at three different temperatures have to be combined leading to a system where at least one of the sensors is insensitive at one of the temperatures.⁶ A SnO₂-based gas sensor is very sensitive to HF,⁷ but because of its very poor selectivity a prior separation step using a gas chromatographic micro-column is required.⁸ Since the latter two instruments are not portable, their application for personal exposure measurements is not yet possible.

Wolff *et al.*⁹ developed a photo-acoustic spectrometer, which uses a single frequency diode laser for selective excitation of trace gases. The photo-acoustic cell together with a semiconductor laser form a compact and relatively cheap gas detector, but further developments are needed to make it useful as a sensitive portable detector for HF in workplace atmospheres. Hoke¹⁰ built a real-time analyser, in which a fluoride ion-selective electrode measured the fluoride ion concentration in an aqueous trapping solution after extraction of HF and particulate fluorides from the air passing through the instrument.

The application of such detectors under workplace conditions for measuring personal exposure to HF has, however, many limitations. Commercially available electrochemical sensors are small and convenient portable instruments, but these sensors can have considerable cross-sensitivities to other gases and vapours (*i.e.* hydrogen chloride (HCl) and sulphur dioxide (SO₂)).¹¹ This makes the use of such sensors difficult in aluminium smelters since HF and SO₂ coexist in pot room air.

Stationary gas monitors using tuneable diode laser absorption spectroscopy (TDLAS) designed by Linnerud *et al.*¹² can be applied for monitoring O₂, carbon monoxide (CO), ammonia (NH₃), HCl and HF in different workplace atmospheres. The designers confirmed that these monitors are capable of measuring gases and vapours continuously in the process industry with fast response times and without known interference from other gases or airborne particles. By automatic compensation for temperature and pressure effects it was possible to overcome such problems as line broadening or frequency drift of the diode laser. Important areas of application for these spectrometers are continuous emission monitoring, process and product quality control. Such instruments have recently been developed for personal portable monitoring. The spectrometer for real-time measurements of HF used by

Dando *et al.*¹³ is also based on tuneable diode laser technology. This spectrometer offers a wide linear dynamic range (0.1–1300 ppm), has a relatively low detection limit (approx. 0.1 ppm) and is capable of measuring short-term peak HF concentrations, but the instrument is not really portable, weighing approximately 15 kg. A later version of the instrument offers nearly the same sensitivity with reduced weight (approx. 7 kg) which still is too heavy to be considered as a practical portable instrument.

Based on the design described by Linnerud *et al.*,¹² Neo Monitors AS in Lørenskog, Norway has, in collaboration with the present authors, developed a portable laser-based HF specific spectrometer with the time resolution and sensitivity required for peak exposure event characterisation. In this study, this novel instrument together with a portable direct reading aerosol spectrometer has been combined with the picture mix and exposure (PIMEX) strategy in order to investigate situations in aluminium smelter pot rooms in which simultaneous peak exposure to HF and particulate matter in the thoracic aerosol sub-fraction occurs. PIMEX is a method for exposure visualisation where video and exposure monitoring are combined.¹⁴

Experimental

Instrumentation

Picture mixed exposure. A PIMEX 2008 system was used for the visualisation of the HF and aerosol exposure in real time. The PIMEX 2008-technique is based on a standard computer and specially developed software. This PIMEX 2008 software is able to record video and data, where the picture from the video camera (cable online) and telemetrically transferred data from the analogue output (0–5 Volt) of the direct reading instrument are presented on the computer screen in real-time and stored on the computer. Telemetry for wireless transmission of monitoring signals from the real-time instruments is essential since it allows workers to move around freely.

After recording, the synchronized video and instrumental signals may be replayed in their original form or be re-processed for subsequent presentations. Recorded and stored sensor data can also be exported to spreadsheet programs such as MS Excel® for further processing. The maximum free range distance for the telemetric system is 1500 metres.

The telemetric sender and the real time HF and aerosol spectrometers were carried in a fireproof backpack by the operators. The telemetric receiver was connected to the computer by two USB cables. The PIMEX 2008 system is capable of handling up to eight different simultaneous incoming analogue signals to be synchronized with the RGB video signal. The high electromagnetic field present in aluminium pot rooms mandated the use of a video camera and a computer system capable of operating under such conditions. A specially designed Panasonic Toughbook CF-30 portable computer with an embedded controller and a SSD-disk together with a Canon HF100 Camcorder were used in this study.

Portable aerosol spectrometer. The DustTrak 8520 (TSI Inc., Shoreview, MN, USA) is a portable, battery-operated, direct-reading aerosol spectrometer incorporating a light scattering

laser photometer. It provides real-time measurements based on 90° light scattering by particles present in air passing through the scattering cell at constant flow. The scattered light intensity determines the particle mass concentration based on an instrumental calibration factor. A continuous analogue output signal allows remote access to real-time particle concentration data, thus making it usable with the PIMEX 2008-equipment. In the present study, particle mass concentrations corresponding to PM₁₀ (thoracic) fraction were measured by selection of the DustTrak 10 µm inlet nozzle with an air flow rate of 1.7 L min⁻¹ and the use of factory calibration settings.

Portable hydrogen fluoride spectrometer. Tuneable diode laser absorption spectroscopy (TDLAS) in the near-infrared has been applied for monitoring HF in workplace air. The measurement principle of TDLAS gas monitors has been reviewed elsewhere.¹⁰ The newly developed LaserGas™ III Portable HF Analyser (Neo Monitors AS, Lørenskog, Norway) is a compact, lightweight, battery powered gas monitor, designed to be operated for an entire working shift without battery recharge. It allows for fast and reliable operation with an adequate dynamic concentration range from sub ppm to several hundred ppm of HF. The detection principle is based on direct absorption with digital second harmonic processing in a Teflon® coated aluminium cell using line tracking on ambient H₂O. This non-contact optical measurement method employs a solid-state laser source, thus the monitor is unaffected by air contaminants and corrosives which reduces the need for regular maintenance. The LaserGas™ III Portable HF updates every second and has a response time (T_{90}) of 10 s. The detection limit for HF is 50 ppb at a gas temperature of 25 °C and a pressure of 1 bar. Since the analogue output is 4–20 mA, incorporation of a 250 ohm resistor to transform the signal into 1–5 Volts is required to comply with the requirements of the PIMEX 2008 system. The required air flow (3.0 L min⁻¹) is maintained by a rotary pump mounted after the absorption cell. The dimensions and the weight of the spectrometer are 110 × 120 × 250 mm and 2.3 kg, respectively. The instrument design and the simplified operating principles are illustrated in Fig. 1 and technical specifications are given in Table 1. The portable spectrometer is also available for other gases, like ammonia (NH₃), hydrogen chloride (HCl) and hydrogen sulphide (H₂S).

Table 1 Instrument specifications for the LaserGas™ III Portable HF Analyser

| | |
|---|--|
| Detection limit | 50 ppb HF ^a |
| Response time, T_{90} | 10 s |
| Averaging time/ measurement interval | 1 s |
| Repeatability | ±1% of reading |
| Optical path length | 250 mm |
| Operating/storage temperature | −20 °C to +55 °C |
| Protection classification | IP65 |
| Analogue output (2) | 4–20 mA current loop, source or sink (500 Ω max. load impedance, not isolated) |
| Digital output | 10/100 Base T Ethernet (Modbus TCP), USB, RS-485 |
| Gas inlet/outlet | 6 mm SMC one touch fittings (series KQG) |
| Inlet air flow | 3 L min ⁻¹ |
| Inlet pressure | ±50 mbar G/0.8 psig |
| Calibration | Check recommended every 12 months |
| Laser class | Class 1 according to IEC 60825-1, eye safe |
| CE | Certified |
| EMC | Conformant with directive 2004/108/EC |
| Dimensions | 110 × 120 × 250 mm |
| Weight (incl. battery) | 2.3 kg |
| Display | 2.8" colour LCD panel (touch screen) |
| Sample cell | Teflon® coated aluminium |
| Battery | Lithium ion battery (14.4 V, 5 A, approx. 10 hour usage per charge) |
| Power consumption | Max. 10 W |

^a At gas temperature/pressure = 25 °C/1 bar.

Site description

Pre-testing of the spectrometers in combination with the PIMEX 2008 equipment confirmed that the instrumentation was operative in the strong electromagnetic field present in aluminium smelter pot rooms.

The PIMEX measurement campaigns for aerosol and HF were conducted in the period October–November 2009 in Søderberg and Prebake aluminium smelter pot rooms, respectively.

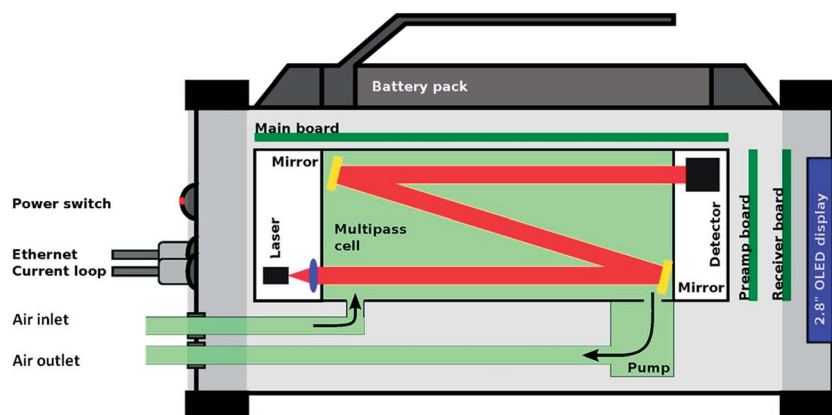


Fig. 1 LaserGas™ III portable HF, simplified design and operating principle.

Based on consultations with the smelters' occupational hygienists different work areas and job tasks were selected for visualisation and identification of peak exposure events.

All measurements were conducted with a volunteer pot room operator carrying the equipment in a fire proof backpack while two of the present authors operated the Camcorder and the receiving Panasonic Toughbook portable computer. The inlets of the Teflon® tubes connected to the spectrometers were placed in the breathing zone of the pot room operator. For scientific evaluation the recorded synchronised HF and aerosol mass concentrations were also imported to MS-Excel®.

Results and discussion

HF and aerosol mass air concentration data obtained in the field measuring campaign were exported to MS-Excel® and plotted in Fig. 2 and Fig. 4–7. To prevent contamination of the absorption cell and the sampling pump by particles, a 37 mm closed-face filter cassette (M000037A0, Millipore) equipped with a 5.0 µm PVC membrane filter (PVC5027000, Millipore) was

mounted at the inlet of the spectrometer. This filter caused peak broadening and reduced the intensity of the HF air concentration signal as illustrated in Fig. 2. All further measurements were therefore made without use of a particle inlet filter. The producer of LaserGas™ III Portable HF has, however, later added a different inlet filter which has been shown not to cause these effects.

The regular need for changing the anode skirt in the Søderberg technology has been identified by the industry to be one of the job tasks generating very high air concentrations of HF and particulate matter.¹⁵ The measured concentrations correspond well to the work operation and the time spent close to the open part of the Søderberg cell. The same source can be assumed for both HF and aerosol as the HF and aerosol concentration data are highly correlated. This is clearly shown in Fig. 2 where both air contaminants are simultaneously present at very high peak concentrations. The peak concentrations for both HF and aerosol exceeded the pre-selected maximum concentration values of 30 ppm and 100 mg m⁻³ for HF and aerosol, respectively. Since PIMEX 2008 also visualises the positioning of the worker(s) to the emitting source and the work procedure, the detailed causes of the peak exposure events could be identified (Fig. 3). This has contributed to improved in-plant technical and work procedures for this Søderberg cell maintenance requirement.

In Fig. 4 the operator carried out an inspection round in a Søderberg pot room. During this work task several simultaneous peak exposure events occurred when walking along the pot line. The highest air concentrations of both PM₁₀ and HF were identified when the operator stayed close to a cell during maintenance for crust removal and preparing for anode skirt replacement. The highest air concentration of HF the worker experienced in his breathing zone was about 20 ppm with a corresponding PM₁₀ value of 9–10 mg m⁻³. This event lasted for about 50 s and when the operator slightly changed his orientation at the same cell, another almost similar peak event occurred.

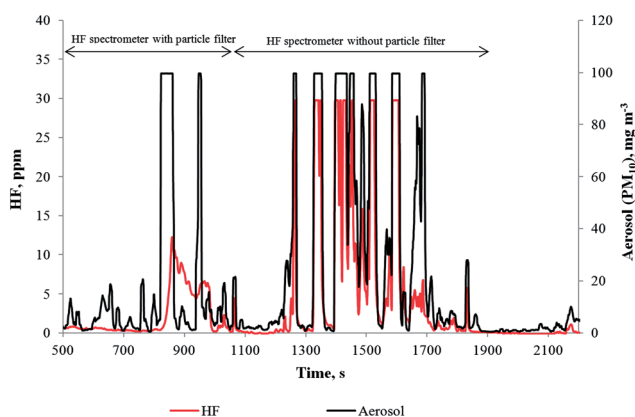


Fig. 2 Anode skirt changing on a Søderberg cell.

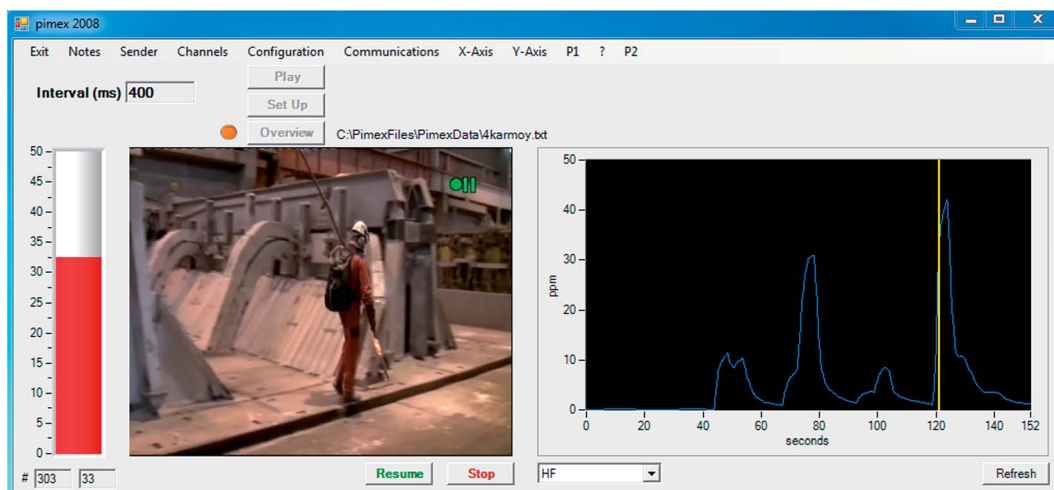


Fig. 3 The PIMEX program screen of the operator walking with a burning wooden stick with bath residues and HF air concentrations. The yellow vertical line is synchronized with the video.

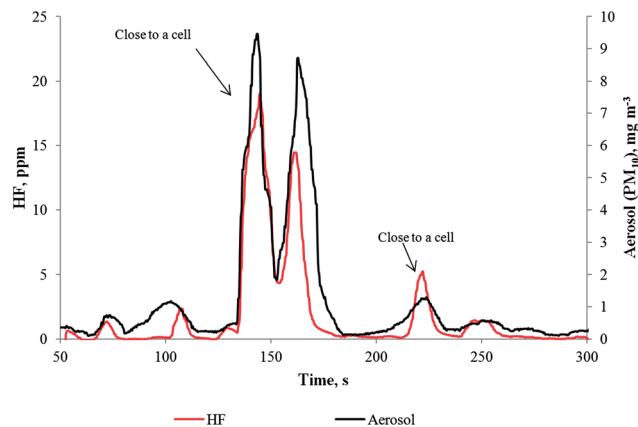


Fig. 4 Inspection round in a Søderberg pot room.

In a Prebake pot room the background air concentrations of PM₁₀ and HF are lower (Fig. 5) compared to the Søderberg pot room (Fig. 4). When the operator was walking around in the Prebake pot room, exposure to PM₁₀ and HF occurred when he was close to tubs containing hot crust/bath residues. This exposure event only occurred when he was positioned between the tubs and the Prebake cells. Thus, it is of paramount importance for the operators to identify both their positions with respect to emission sources of PM₁₀ and HF and to the ventilated air direction in the pot room (Fig. 5).

When the covers were removed from the cells the operator was only marginally exposed to PM₁₀ and HF while covering the replaced anodes with a mixture of alumina and crushed bath residue, showing a high ventilation efficiency of the cell (Fig. 6). The PM₁₀ air exposure events occurred during manual repositioning of the cell covers which were contaminated with a mixture of alumina and crushed bath residue which had been fed to the cell by the crane operator. The main HF exposure events illustrated in Fig. 6 were, as previously discussed, associated with the positioning of the operator relative to hot bath residue in tubs, on replaced anodes or in crane grabs.

Most surprisingly no exposure to PM₁₀ or HF was registered when the operator was preparing for siphoning off aluminium metal by poking a hole in the Prebake cell crust with a

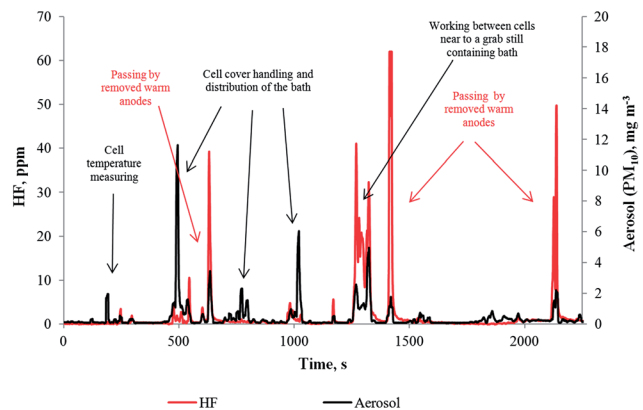


Fig. 6 Anode exchange in a Prebake cell.

traditional wooden stick. Considerable exposure to both contaminants occurred while the operator was moving from one cell to another in the pot line carrying the wooden stick which was contaminated with hot bath residue and was partly burning. This occurred only when the operator carried the tool in front of himself as illustrated in Fig. 7.

The use of Søderberg technology has been terminated in all but one of seven smelters in Norway during the last decade. In the present study it has been shown that HF and the PM₁₀ aerosol sub-fractions are measured in Prebake pot room air in areas where hot bath residues and hot replaced anodes are located. These air contaminants are most likely formed by evaporation of fluorides from the electrolyte residues and their reaction with hydrogen containing components (*e.g.* water vapour present in the pot room air). The measurements showed also that the air concentrations were considerably lower in the breathing zone of the operator(s) when exchanging anodes with uncovered cells and enforced ventilation. In order to prevent the simultaneous exposure to HF and PM₁₀ among workers it is important to visualize for all pot room operators that being close to these hot residues may cause high peak exposure under unfavourable ventilation. Further, the storage of hot residues outside the electrolytic cell without any point source ventilation should be avoided.

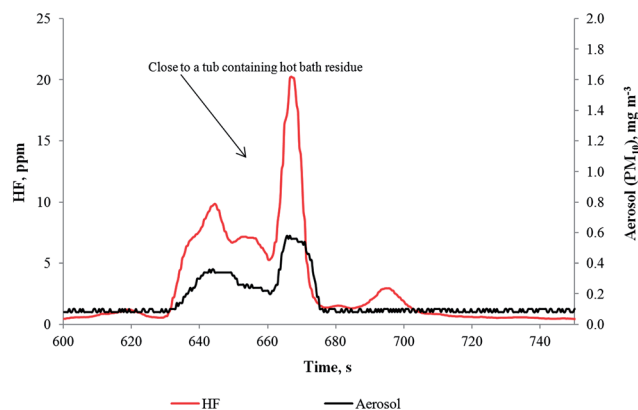


Fig. 5 Inspection round in a Prebake pot room.

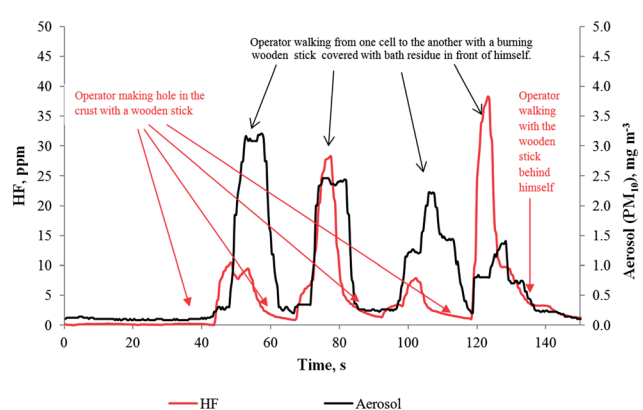


Fig. 7 Preparing for siphoning off aluminium in a Prebake pot room.

Conclusions

The PIMEX 2008 system combined with the novel HF and aerosol real-time portable spectrometers is a versatile tool for visualisation and identification of peak exposure events in aluminium smelter pot rooms. The HF spectrometer performed well under the extreme conditions in the pot rooms. The PIMEX method allows the main sources of aerosol and HF exposure to be identified and explained. In Søderberg technology the exposure to PM₁₀ and HF occurred when the operators were positioned next to cells with a partly removed crust. In Prebake pot rooms several sources were identified. Considerable amounts of HF and PM₁₀ particulate matter were simultaneously emitted during storage of hot replaced anodes and bath residue.

Acknowledgements

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