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Peak exposures in aluminium potrooms: instrument development and field calibration†

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Aluminium smelter potrooms are unique in that workplace exposures to hydrogen fluoride (HF), sulfur dioxide (SO_2), and particulate matter occur simultaneously for some tasks. The peak exposures to these contaminants are of increasing interest in discovering the etiology of respiratory health effects. While a variety of direct-reading instruments are available for sulfur dioxide and particulate matter, only a few exist for hydrogen fluoride. The sensors in these HF instruments have a cross-sensitivity to sulfur dioxide making it difficult to monitor HF in an environment that also contains SO_2. To overcome this problem, we assessed the simultaneous use of two electrochemical instruments: one with a SO_2 sensor that does not respond to HF and the second with a hydrogen fluoride sensor that responds to both HF and SO_2 in a 1 : 1 ratio, termed 'total acid gas'. The difference in the response between the two instruments should indicate the HF concentration: [HF + SO_2] minus SO_2 equals HF. The performance characteristics of this sampling train were evaluated in the laboratory through the generation of both HF and SO_2 with permeation tubes. The response and recovery times for the SO_2 only instrument were acceptable (6 and 15 s, respectively), but the "total acid gas" instrument exhibited both slow response and slow recovery approaching three and six min. The association between the traditional integrated filter sampling method and the direct-reading instrument for SO_2 is 0.80 (Spearman's *rho*). The use of the digital filter strengthens the association between the HF direct-reading instrument and the integrated samples from 0.41 to 0.68.

1. Introduction

The association of asthma with work in aluminium smelters first entered the literature in the 1930's indicating that asthma was more frequent in the workers of Norwegian smelters than the surrounding community.[1] Current estimates of the incidence of this so-called "potroom asthma" range from 0.06 percent per year for workers in North America to 4 percent per year for European workers. The reason for this large difference in incidence rates has not been elucidated, but it has been suggested that it may be due to variations in pre-employment screening, diagnostic techniques, or level of environmental exposures partly related to climate.[2] Although the reported symptoms and lung function changes in potroom workers are similar to sensitization asthma, few potroom workers have elevated eosinophils or IgE as occurs in sensitization asthma. Soyseth and Kongerud[3] reported the increased prevalence of respiratory and asthmatic symptoms as well as abnormal lung function for potroom workers with exposures greater than 0.5 mg m^{-3} total fluoride. A more recent epidemiological study[4] in smelter potrooms indicated a dose–response relationship between fluoride exposure, as measured by plasma fluoride levels, and bronchial hyper-responsiveness. O'Donnell[5] has also suggested the combined exposure to the irritant gases sulfur dioxide and hydrogen fluoride, especially with the potential for high peak exposures, contributes to respiratory disease in potrooms.

The electrolytic reduction of aluminium occurs in a steel cell or 'pot', which contains a mixture (or bath) of cryolite, fluorspar (CaF_2) and aluminium fluoride (AlF_3) to which alumina is added periodically.[6] The anode consists of a combination of petroleum coke and coal tar pitch that can be utilized as either a pre-baked consumable block (pre-bake process) or as an anode paste (Soderberg process).[7] A low voltage, high amperage electric current passes through the cryolite–alumina mix to power the reaction.

Carbon monoxide is created during the incomplete combustion of carbon in the anodes while the oxidation of residual sulfur in the anode generates sulfur dioxide. Hydrogen fluoride as well as soluble particulate fluoride are generated by a secondary reaction:[6]

$$2Na_3AlF_6 + 3H_2O \rightarrow Al_2O_3 + 6NaF + 6HF$$

Until recently, only vague reports[8] provided information on maximum peak exposures to sulfur dioxide ranging from 20 to 30 ppm. Real-time exposure assessment of sulfur dioxide using an electrochemical sensor indicates maximum 2 min averages of 54 ppm during anode replacement in a pre-bake smelter although the average exposure for the task was 1.1 ppm.[9] Instantaneous peaks were as high as 190 ppm for a few seconds during carbon setting. Little if any information is available for peak hydrogen fluoride exposures due to the lack of personal direct-reading instrumentation. All current portable/personal hydrogen fluoride instruments utilize electrochemical sensors that respond to sulfur dioxide making it impossible to differentiate between the two gases when both are present.

The aim of this investigation is to use two direct-reading instruments to develop a family of peak exposure metrics that incorporate the magnitude, duration, and frequency of peak exposures to the acid gases HF and SO_2 as well as to particulate matter. As a first step toward this goal, this paper describes the development of a system for simultaneous use of two electrochemical instruments to determine the HF concentration. One instrument is a passive SO_2 sensor that does not respond to HF, and the second instrument uses active sampling with a hydrogen fluoride sensor that responds to HF and SO_2

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in a 1 : 1 ratio, termed a "total acid gas sampler" (TAG). The difference in response between these two instruments should indicate the HF concentration, *i.e.* $[HF + SO_2] - [SO_2] = [HF]$.

2. Material and methods

2.1. Preliminary studies

The laboratory evaluation was designed to demonstrate the response characteristics of the instruments. Hydrogen fluoride (HF) and sulfur dioxide (SO_2) test atmospheres were generated using permeation tubes and the Model 120 Dynacalibrator (VICI Metronics) equipped with a PTFE (Teflon®) permeation chamber. These atmospheres were generated individually and with both gases simultaneously using Teflon® tubing to deliver the generated concentration to the air sampling instrument inlet. The generated concentrations of HF and SO_2 were determined by pre and post weighing of the permeation tubes after a period (greater than 3 days) of equilibration. This was further confirmed by comparison of the generated concentration results to traditional integrated sampling of the generated atmosphere using standard analytical methods (NMAM 7906 for HF and NMAM 6004 for SO_2). These methods were used during the subsequent field assessment.

We selected a Mil–Ram ToxArray 1000 "Hydrogen Fluoride" instrument as the total acid gas sampler in conjunction with a Metrosonics pm-7700 sulfur dioxide instrument that is specific to SO_2. In an aluminium smelter environment, the Mil–Ram instrument provides a measure of the total acid gas—a combination of both the HF and SO_2 concentration with a measurement range of 0.1–20 ppm. Although it does not have intrinsic data-logging capability, it does offer a recorder output (0–2 V) that is suitable for data-logging. A Metrosonics 1100 data-logger was utilized with an adapter connector cable supplied by Metrosonics. Although marketed as a hydrogen fluoride sensor, the cross-sensitivity information provided by the company indicates that it responds equivalently to both HF and SO_2, *i.e.*, a 1 : 1 ratio. The manufacturer's reported response/recovery times were 45 and 30 s, respectively.

The Metrosonics pm-7000 personal data-logging instrument is equipped with an electrochemical sulfur dioxide sensor (City Tech Model 7 ST/F). This sensor uses a capillary diffusion barrier to control airflow to the electrode and exhibits a measurement range of 0.2–200 ppm with a display resolution of 0.2 ppm. The instrument and sensor manufacturer report that this SO_2 sensor does not respond to either hydrogen chloride or hydrogen fluoride and has a response time of <35 s.

The simplest sampling train for the combined instruments involved operating the instruments in series using the pump of the Mil–Ram to draw air into both instruments, through the Metrosonics sensor first and then through its own sensor, using Teflon®-lined tubing. The inlet of the Metrosonics instrument was connected to the Teflon tubing from the generator using an approximately one inch section of clear PVC (Tygon®) tubing minimizing the exposed surface of the Tygon® to the air stream.

Initial low recovery of HF using a standard polystyrene cassette as a comparison method suggested that HF was reacting with polystyrene. Switching to a custom-made 3-stage Teflon cassette alleviated this loss. Table 1 illustrates that there was a 70–80% loss of HF for the polystyrene cassette during the laboratory trial, which was confirmed in preliminary field trials.

Loss of HF or SO_2 along the sampling train did not occur as confirmed by allowing the Mil–Ram to stabilize at a challenge concentration and then adding the Metrosonics sensor to the sampling train. This addition did not result in a noticeable change in the response of the Mil–Ram.

Table 1 Hydrogen fluoride recovery comparison between polystyrene and Teflon cassettes reported as mean value of 3 samples per exposure level

Known HF (ppm)	Teflon cassette (ppm)	% Recovery Teflon	Polystyrene cassette (ppm)	% Recovery polystyrene
4.0	4.7	118	2.7	68
7.0	7.7	110	5.6	80
13.6	14.4	106	11.7	86

Modification of the instruments was necessary for them to operate in series as active samplers. Affixing the calibration cap to the sensor head with an internal Teflon gasket and sealing the zero and span ports accomplished active sampling with the SO_2 specific instrument. However, the internal pump of the Mil–Ram operates at a higher flow rate (350 ml min^{-1}) than the recommended calibration rate of the Metrosonics (200 ml min^{-1}). Varying the flow rate through the Metrosonics sensor over a range of 200–400 ml min^{-1} did not change its response to a 12 ppm challenge concentration. Above 500 ml min^{-1}, the instrument read lower than 12 ppm due to leakage of clean air around the calibration cap.

The performance characteristics of the instruments were assessed including specificity and sensitivity of the sensors, stability of the response, instrument linearity, and response time. The specificity of the SO_2 sensor is presented in Table 2 where the addition of HF to the sampled stream does not influence sensor response indicating that the SO_2 sensor was specific to SO_2 as reported by the manufacturer.[10]

When allowed sufficient time to reach their maximum response level, both instruments displayed a linear response between 0 and 20 ppm as depicted in Figs. 1 and 2 with a correlation coefficient and regression intercept approaching 1.0 for both SO_2 and HF. This was true for the acid gas instrument when exposed to HF individually as well as to mixed gas environments of HF and SO_2 indicating the acid gas instrument was sensitive to both HF and SO_2 as expected at a 1 : 1 ratio.

The limit of detection (LOD) and limit of quantification (LOQ) for the instruments was calculated using the International Union of Pure and Applied Chemistry method of 3 or 10 times the standard deviation of blank (zero) samples divided by the linear regression slope.[11] For the Metrosonics sensor, the LOD is 0.1 and the LOQ is 0.3 ppm; for the Mil–Ram, 0.01 and 0.04 ppm. The Mil–Ram instruments demonstrated very little zero drift resulting in a LOD and LOQ lower than the display resolution of the instrument.

Each instrument's response time was determined as the time from initial exposure to the atmosphere to the time the instrument reached 90% of the expected concentration. The recovery time determination begins when the instrument is removed from exposure and ends when the instrument reaches 10% of the starting concentration. The response and recovery times for the SO_2 only instrument were acceptable and consistent with the manufacturer's specifications at 6 and 15 s, respectively. Fig. 3 contrasts this quick response time of the SO_2 instrument with the substantially slower response time of the total acid gas instrument as depicted by the bold lines.

Table 2 Cross-sensitivity of the SO_2 sensor to HF (ppm)

Known HF	Known SO_2	Active response	% of known
1.2	1.4	1.4	100
1.6	1.8	2.0	111
2.2	2.6	2.8	108
4.3	5.0	4.9	98
8.8	9.5	9.4	99

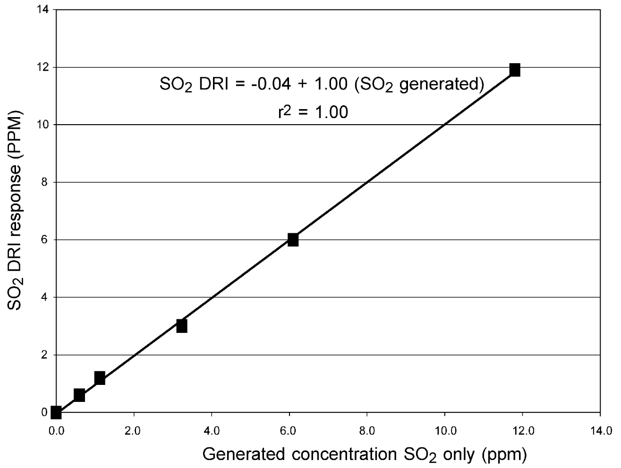

Fig. 1 Linear response of SO_2 only instrument to known concentrations of SO_2 (ppm).

The total acid gas instrument has a slow response and recovery time to SO_2 (3 and 8.3 min) and even slower to HF at 6 and 20 min, respectively. The response time for HF is lower than the manufacturer's specifications, but is consistent with reports in the literature.[12] If the SO_2 sensor responds more quickly to peak concentrations of SO_2 than the total acid gas instrument, subtracting the SO_2 response from the total could often result in negative HF concentration calculations. Therefore, it was crucial to compensate for this difference in response time between the two instruments before we could move further with personal sampling. The use of a digital filter was thought to be able to 'slow' the SO_2 instrument's signal to match the response time of the HF/SO_2 sensor. A digital filter is a computation that takes a sequence of numbers (input) to produce a new sequence of numbers (output) and is an application of autoregressive moving average models.[13,14] The order of a filter is the number of previous inputs needed to generate the new output where a first order moving filter average is

$$y_{(t)} = (\alpha_1 x_{(t)} + \alpha_2 x_{(t-1)})$$

where $y_{(t)}$ is the output of the digital filter, $x_{(t)}$ is input or the sampled SO_2 value at time t and α_1 and α_2 are filter coefficients specific to the digital filter. If the output of the filter relies solely on input values it is non-recursive.[14] Recursive filters are also of use where the output uses previous output values so that previously calculated output values go back into the calculation of the current output requiring two sets of filter coefficients (α_1, α_2 and β_1, β_2).

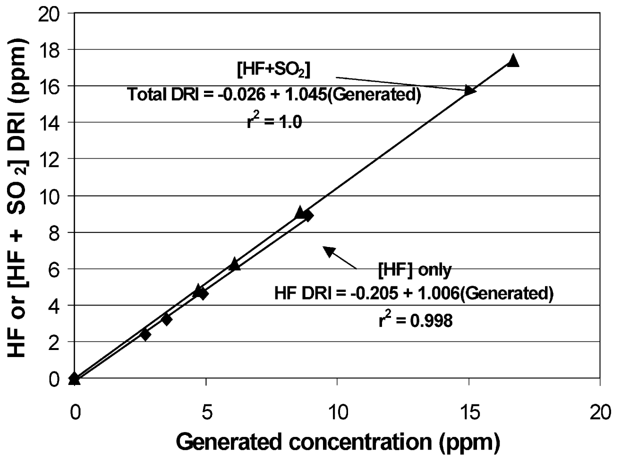

Fig. 2 Linear response of Total Acid gas instrument to HF and $[HF + SO_2]$ (ppm).

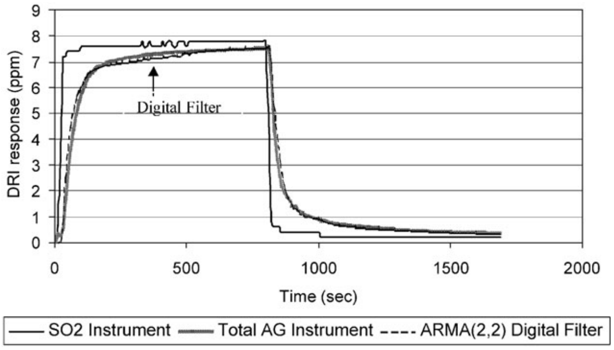

Fig. 3 Digital filter applied to the SO_2 instrument to match the TAG response (Step response to 7.8 ppm SO_2).

For the two instruments in this study, a second order recursive digital filter (represented in Fig. 3 by the dashed line) was necessary to account for their different response characteristics. The digital filtered version of the SO_2 instrument closely overlays that of the total acid gas response so it is difficult to see although a small difference in the signal may be evident at the arrow.

The filtered output[15] is calculated as follows

$$y_{(t)} = \beta_1 x_{(t-2)} + \beta_2\, x_{(t-1)} + \alpha_1 y_{(t-2)} + \alpha_2 y_{(t-1)}$$

where

β_1 and β_2 = coefficients for the input values at $t - 2$ and $t - 1$, respectively

α_1 and α_2 = coefficients for the previous output values

The β coefficients are the prime adjustment to the SO_2 signal input while the α coefficients serve to provide a feedback mechanism to the filtered output as a fine adjustment.

The calculation of the HF concentration then becomes

$$[HF + SO_2] - SO_{2(\text{filtered})} = HF_{\text{calculated}}$$

Table 3 clarifies this process with some example values where $SO_{2(t)}$ is the input for the digital filter (the original SO_2 sensor response) and $SO_{2\text{filtered}(t)}$ is the output of the second order recursive digital filter described above.

The $SO_{2\text{filtered}}$ values are subtracted from the total acid gas instrument reading at time t, giving the calculated HF value at time t.

2.2 Field studies

Study design and subjects. The instrument evaluation took place in three aluminium smelters in the United States all of which use the pre-bake technology although with minor variations in the process and pot design. This allows the assessment of a range of possible exposure combinations of acid gases and particulates given the different technologies employed in the smelters. The sampling strategy was task-based covering eleven common tasks in aluminium smelter potrooms as listed in Table 4.

The exposure assessment consisted of the real-time measurement of SO_2 and total acid gas along with integrated sampling

Table 3 HF calculation method with the digital filter applied to the SO_2 instrument (ppm)

$\text{Time}_{(t)}$	$SO_{2(t)}$	$SO_{2\text{filtered}\,(t)}$	Total Acid $\text{gas}_{(t)}$	Calculated $HF_{(t)}$
1	0.1		0.2	0.1
2	0.1		0.2	0.1
3	0.2	0.10	0.4	0.3
4	0.2	0.21	0.4	0.19
5	0.7	0.19	1.3	1.1
6		0.73	1.0	0.27

Table 4 General job and task titles in aluminium smelter potrooms

Job	Task
Carbon setter	Covering anodes
	Crust/line breaking
	Anode change
	Clean-up
Potman	Pot jacking
	Dressing pots
Tapper	Aluminium tapping
	Bath tapping
Crane operator	Anode change
	Tapping

methods for SO_2 and HF. Each of three workers per task was asked to participate by wearing the instruments on two occasions, preferably on different days.

The sampling train weighed approximately 3 pounds and was secured at the worker's waist in a belt pack with a sampling line routed into the worker's breathing zone. The pumps were calibrated at a flowrate of 1.5 l min^{-1} using the customized Teflon air-sampling cassette as discussed in the lab evaluation section. The SO_2 sensor was directly in the breathing zone with a sampling line connecting it to the total acid gas monitor/sensor located in the belt pack. Each task was monitored for approximately one hour, but occasionally less depending upon the cycle time of the task.

The direct-reading instruments were downloaded between each sampling period while changing the Teflon cassette for the integrated sampler. Calibration of the acid gas direct-reading instruments occurred through side-by-side integrated sampling using carbonate-treated back-up pads with a 0.8 µm MCE pre-filter (NIOSH Method 7906 and 6002 for HF and SO_2, respectively). The MCE pre-filter removes particulate fluoride from the air stream prior to contact with the carbonate-treated pad so particulate fluoride contamination of the HF result isn't likely. Some reports have suggested the potential for the particulate on the MCE pre-filter to scrub HF upstream from the carbonate-treated pad resulting in low HF values. The laboratory used standard quality control procedures for analyzing the integrated samples during the laboratory analysis including laboratory spikes and generation of a standard curve. The first plant had air concentrations lower than expected resulting in a few integrated samples that were below the LOD/LOQ. Modifications of the sampling protocol to sample at 1.5 l min^{-1}(increased from 1.0 l min^{-1}) as well as conducting the work in plants with higher exposures reduced the number of integrated samples that were less than the LOD for most tasks.

Preliminary assessments in the workplace identified the possibility of heat-related drift of the SO_2 sensor since the sensor was located in the breathing zone directly exposed to radiant heat from the pots. The drift issue was largely corrected by covering the black-colored SO_2 sensor with aluminium foil to reflect the heat since we were not able to isolate it from the atmosphere, as we were able to do with the total acid gas monitor. In some instances, peaks are above the 0–20 ppm range of the total acid gas instrument. Due to the slower response time of this instrument, the peaks must last a sufficient length of time or be very high (~50 ppm) for the effect to be noticed dramatically.

3. Results

In total, seventy-five samples were collected within four primary tasks (carbon setting, crust/line breaking, tapping, and dressing pots) with five samples lost: one filter sample and four direct-reading results. Five additional samples were removed from the HF analysis due to extended periods of over-range output largely due to high SO_2 concentrations that are beyond the range of the total acid gas monitor.

3.1 Drift

Initial examination of the direct-reading instrument data indicated some baseline drift during the sampling periods. Heat is most likely the cause for the SO_2 instrument drift since the instrument would frequently not return to the baseline even though the workers were periodically in the aisles that have low contaminant concentrations (<0.2 ppm). This drift was generally progressive over the sampling time with one example having a baseline drift from 0 to ~1.8 ppm. The total acid gas instrument did not appear to be affected by the heat related drift. Any observable drift is more likely a result of concentration spikes combined with its slow recovery time.

We assessed the use of a variety of methods to correct for this drift using a software program (written in AWK)[16] as well as a subjective baseline adjustment of each sample. For both acid gas instruments, these correction methods did not increase the correlation with the integrated sample results nor move the regression coefficients closer to one or the intercepts closer to zero and are therefore not included in this discussion. Details of this analysis and the use of a baseline correction for the particulate data will be reported elsewhere.[17]

3.2 Comparison between integrated and direct-reading instrument (DRI) data

The distribution of the average concentrations of both direct-reading and integrated task average concentrations was more lognormal than normal. However, correlations between independent variables were performed on the un-transformed data using non-parametric methods to maintain the range and "weight", or importance, of the higher values. The Spearman's correlation coefficient (*rho*) was calculated between the direct-reading and integrated SO_2 concentrations, between the total acid gas ([HF + SO_2]) direct-reading and integrated concentrations, and between the calculated HF concentrations and the HF integrated sample results. The association between the SO_2 sampling methods (Fig. 4) is acceptable ($rho = 0.80$; $p = <0.01$, $n = 66$). In general, the direct-reading results are lower than the integrated samples illustrated by a coefficient (slope) of 0.83 and an intercept less than 0.1. Removing the outlier produces little change in the correlation, but would improve the slope to 0.93 while reducing the intercept to −0.1.

To calculate HF concentration, the digital filter equation was applied to each 10 s reading from the SO_2 instrument. The product of this computation was then subtracted from the total acid gas instrument concentration. Figs. 5a and 5b are

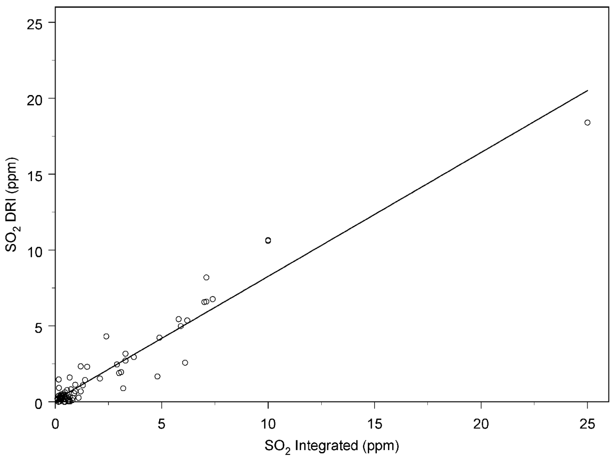

Fig. 4 The association between the SO_2 only DRI and the integrated sample SO_2 ($rho = 0.80$; $n = 66$; $p = <0.01$).

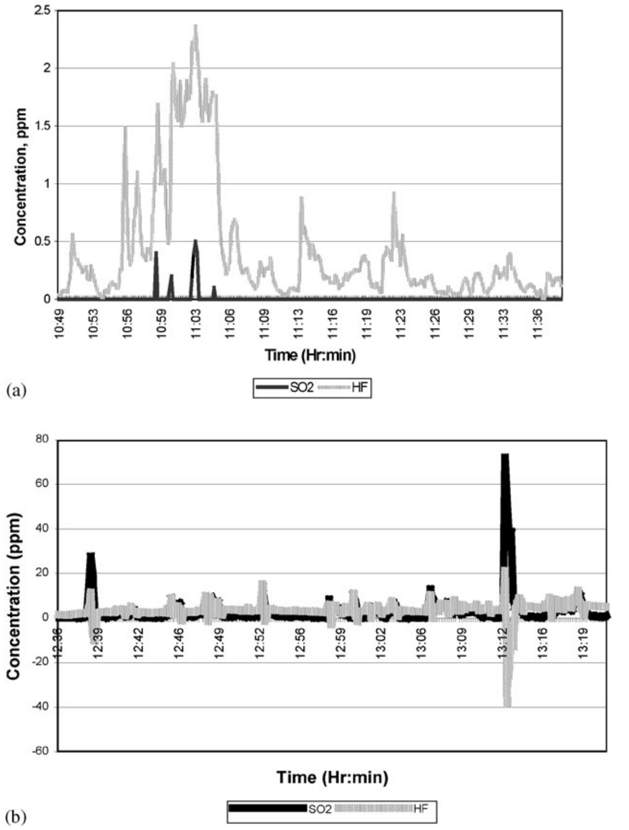

Fig. 5 (a) SO_2 DRI and calculated HF readings for a low exposure task (raising beams); (b) SO_2 DRI and calculated HF readings for a high exposure task (line breaking).

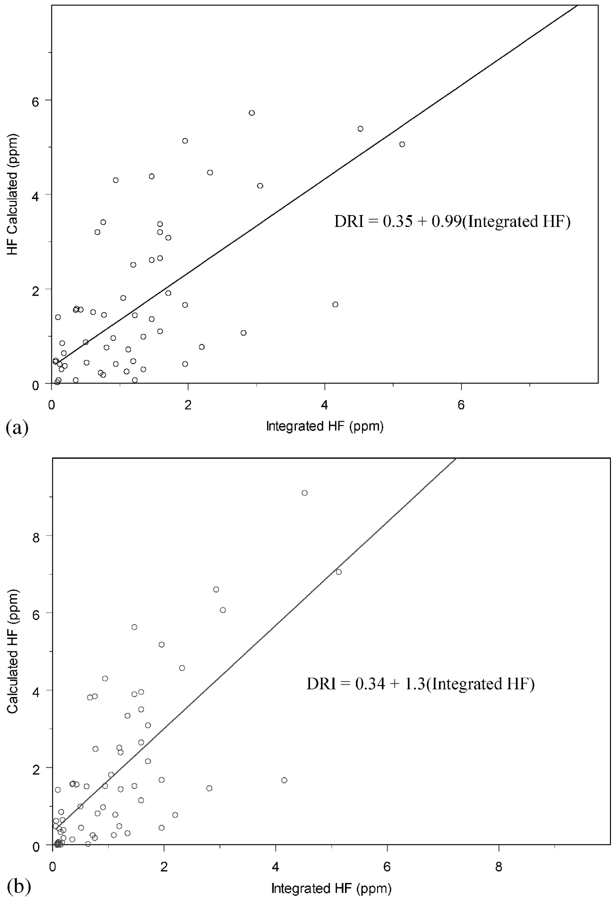

Fig. 6 (a) The association between the HF calculation method (using only the digital filter) and the integrated sample (*rho* = 0.68; $p = <0.01$; $n = 64$); (b) The association between the HF calculation method (using the digital filter and truncating) and the integrated sample (*rho* = 0.72; $p = <0.01$; $n = 64$).

examples of instrument responses for two different tasks. For lower concentration tasks similar to raising beams in Fig. 5a, the calculated HF concentration is relatively straight-forward. However, for tasks with higher peak exposures (Fig. 5b), especially to SO_2, the digital filter computation occasionally results in negative HF concentrations. As an interim step in addressing these negative values, we also tried truncating the digital filter calculation replacing all negative values with a zero reading.

The relationship between the integrated and non-truncated (includes negative values) calculated direct-reading HF concentrations is depicted in Fig. 6a showing a correlation of 0.68.

The correlation (Fig. 6b) between the integrated and calculated DRI HF concentrations improved slightly to 0.72 when the truncated values were included with the regression components with little change in the intercept, but an increase in the slope to 1.3.

3.3 Additional predictors

Additional independent variables were added to the regression analysis for both SO_2 and HF method comparisons. For HF, plant is a significant modifier and improves the *r*-squared value from 0.53 to 0.67 explaining 14% more of the variability. The coefficient of the regression equation also improves to 1.01 although the intercept increases to 0.60.

4. Discussion

The study describes the development of the use of two direct-reading instruments to indirectly measure peak HF concentrations in aluminium smelter potrooms. Potrooms are challenging environments for direct-reading instrumentation due to their mix of contaminants, high peak exposure possibility, potential for electromagnetic field interference, and extreme temperature fluctuations where the aisles can be below freezing depending on outside temperature while activities on the raised pots involve high ambient and radiant heat. The SO_2 only instrument performed well although is sensitive to heat with its current black-colored sensor housing. The use of aluminium foil or another reflective coating/paint can lessen the drift associated with this heat. In the present sampling arrangement, the total acid gas monitor is protected in a belt-mounted pouch, which usually faces away from the direct heat source. High peak exposures can be problematic with the limited range of the total acid gas instrument and they may also cause drift, as the instrument cannot quickly return to baseline.

The HF calculation method provides at least a relative concentration of HF peaks and identifies how frequently these peaks occur. Directly calculating HF from the SO_2 and total acid instruments without baseline correction provides poor correlations with integrated sampling largely due to the slower response time of the total acid gas instrument to SO_2. Applying a digital filter to the SO_2 instrument successfully ameliorates the difference in response times. The acid gas instrument is also slow in responding to HF alone, but this should mainly result in the DRI not achieving the maximum concentration of the true peak while the area under the curve of the instrument is able to approximate the true average concentration. The importance of location in the multiple regression analysis could suggest that the instrument(s) were behaving differently over the course of the investigation (1.5 years) or, more likely, that the total acid gas instrument response is dependent on the exposure levels. For the three plants investigated, one had relatively high exposures compared to the other two while another had substantially lower concentrations both in their peak as well as average values.

This approach for the real-time measurement of hydrogen fluoride is feasible, but is limited by differences in sensor response/recovery times and the need to use multiple instruments for analysis and data-logging.

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