

# Evaluation of methodologies for assessment of SO<sub>3</sub> concentration in industrial off-gas

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## Abstract

Assessment of acid dew point in industrial off-gas has become increasingly important with strategies for heat recovery and use of more concentrated gas compositions. Several approaches to acid dew point assessment makes use of glassware not compatible with the high fluoride concentrations found in unfiltered gas. In this work, a new and simplistic approach to acid dew point assessment is evaluated side by side with conventional methodology. The new approach captures SO<sub>3</sub> in the gas as sulfate onto solid NaCl trap. Interference from SO<sub>2</sub> is avoided since it passes through the NaCl trap unreacted. The trap is then dissolved in water for direct analysis of the by ion chromatography. The importance of isokinetic sampling was evaluated, and no significant difference in results was observed. This suggests that the acid droplets are small. The method is shown to be promising for acid dew point assessment in industrial off-gas.

Keywords: acid dew point, off-gas monitoring, ion chromatography

## Introduction

The primary off-gas composition in aluminium production have been extensively studied. Whereas the absolute concentration levels may change with air dilution, the relative concentration between gas constituents remain fairly constant (Aarhaug & Ratvik, 2019). Less studied is the presence of SO<sub>3</sub> in the off-gas, this because conventional methods for assessment involves use of glassware not compatible high concentration of HF in the off-gas.

Sulfur trioxide in off-gas is believed to be the result of oxidation of SO<sub>2</sub>. Conversion is strongly temperature dependent, and slow due to kinetics (Solheim, 2022) and often assumed to be in the range of 1 to 5 % (Schnelle Jr et al., 2015). Conversion is further known be catalyzed by impurities like V and Fe known to be present in the carbon anodes (Kramer et al., 2012). SO<sub>3</sub> is hygroscopic and at temperatures below 400 °C will react with water to form sulfuric acid.

The correlation between SO<sub>3</sub> concentration and acid dewpoint depend on the SO<sub>3</sub> concentration and humidity (Verkhoff, F.H.; Banchemo, 1974)(Okkes, A.G.; Badger, 1987). More recently machine learning was applied to improve the prediction (Zarenezhad & Aminian, 2011):

$$\theta_{\text{dew}} = 150 + 8.1328 \cdot \ln(p_{\text{H}_2\text{O}}) + 11.664 \cdot \ln(p_{\text{SO}_3}) - 0.38226 \cdot \ln(p_{\text{H}_2\text{O}}) \cdot \ln(p_{\text{SO}_3})$$

where partial pressures are in mm Hg and temperature in °C. Traditionally, SO<sub>3</sub> in off-gas has not been a problem since concentrations in the gas translates to acid dew points values lower than the actual temperature of the gas and the duct surfaces: corrosion problems are not a common in off-gas ducts. With introduction of

heat exchangers to the off-gas, knowledge of the dewpoint becomes critical if corrosion protection is to be avoided.

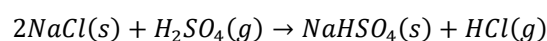
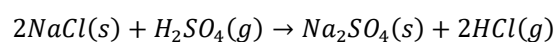
Future scenarios for primary aluminium production with carbon as a reducing agent must include efforts to capture CO<sub>2</sub> emitted. With today's concentration in the off-gas in the range of 0.5-1 % capture is difficult to apply. Efforts to increase the CO<sub>2</sub> concentration in the off-gas has been demonstrated (Lorentsen et al., 2009). More recently, efforts have been made to reduce the air draught by recycling the air and in this way increase the concentration of CO<sub>2</sub> in the gas. The implications have been discussed (Solheim & Senanu, 2020), and gas recycling will also increase concentration of HF and SO<sub>2</sub> in the gas thus exacerbating the problem with acid dew point if heat exchangers is applied to recover the heat. For downstream CO<sub>2</sub> capture with e.g. amine technology, the presence of sulfuric acid aerosols could lead to losses of absorbent due to formation of amine mist (Mertens et al., 2015).

The most widely accepted method for sulfur trioxide analysis is the controlled condensation method (*BS 1756-4 Methods for Sampling and Analysis of Flue Gases Part 4: Miscellaneous Analyses*, 1977). The method is described in more detail in (Gustavsson & Nyquist, 2005). In short, sampled gas are cooled in a condensation column to temperature higher than the water dewpoint but lower than the acid dew point. In this way, sulfuric acid is collected as condensate on the column walls and the sintered glass filter used at the end of the column. By avoiding condensation of water, interference from SO<sub>2</sub> is minimized. After sampling, the glassware is washed with a 5 % vol isopropanol solution that is either analyzed by ion chromatography or by titration. Due to the high hydrogen fluoride content in the off-gas, the use of glassware is not suitable the application discussed in this paper.

Another commonly used method for SO<sub>3</sub> determination is the isopropanol bottle method ("Method 8 Determination of Sulfuric Acid and Sulfur Dioxide Emissions from Stationary Sources," 2019). Gas is passed through gas bubblers filled with 80 % vol isopropanol to capture SO<sub>3</sub>. In order to avoid evaporation of absorbent, the gas bubblers must be cooled to 0 °C with ice or even colder temperatures with a cryostatic bath. Most SO<sub>2</sub> will pass through the bubblers, and for concentration estimation additional gas bubblers filled with 3 % vol hydrogen peroxide can be used. Analysis of the SO<sub>3</sub> can be performed with ion chromatography, inductively coupled plasma mass spectrometry or titration. Since there is some solubility of SO<sub>2</sub> in 80 % isopropanol, slow oxidation of SO<sub>2</sub> dissolved sulfite to sulfate could interfere with the sulfuric acid estimate. Bubbling of absorbent with inert gas and immediate analysis after sampling are arguments that could minimize the interference from SO<sub>2</sub>. Beneficial to the ion chromatographic method is that it allows for evaluation of both sulfite and sulfate peaks of the absorption solution.

Commercially condensation probes have previously been commercially available from Breen and Land. The working principle for the probes is to actively cool the probe with e.g. compressed air so that when it reaches the dew point of the acid, the condensed acid will result in conductance between electrodes embedded on the surface. Thermocouples at the surface is used to estimate the accurate acid dew point. Problematic for application in primary aluminium production is the fact that the probes are made from quartz glass that will degrade in the hydrogen fluoride atmosphere. SINTEF made an attempt to modify a Land Instruments ADM 200 probe using polymeric glass in the probe (Aarhaug & Kjos, n.d.). While the conversion from pyrex was successful it turned out that the heat conductivity of the polymeric glass was too low for efficient cooling with compressed air: the probe could only be cooled to about 80 °C which was not sufficient to estimate the acid dew point.

More recently, a method using solid absorbent has been revisited (Cooper & Ferm, 1994). The principle of the method is to use a salt trap where gaseous sulfuric acid reacts with the sodium chloride to form sodium sulfate and bisulfate according to the reactions:



SO<sub>2</sub> in the gas does not react with the salt and will pass through the trap. Since condensation of water would dissolve the salt and potentially solvate SO<sub>2</sub>, the temperature of the trap is kept well above the dew point of

water. The salt is trapped in a Teflon tube by glass- or Teflon wool if hydrogen wool present. After sampling, salt is dissolved in de-ionized water and analysed by ion chromatography. Evaluation of use of different salts has been documented (Vainio et al., 2013). The method was found to be in good agreement with the controlled condensation method (Fleig, 2012).

In this work, the salt method has been directly compared with the isopropanol absorption bottle method for characterization of the acid dew point in the off-gas at the Hydro Aluminium Smelter at Sunndalsøra. The ion chromatograph at the smelter laboratory was used to analyze the samples immediately after sampling.

## Experimental

Sampling of gas was performed at a regular sampling point, and a standard isokinetic probe from the smelter was used. Two gas treatment centers were sampled from. A sampling pump with a capacity of about 1 m<sup>3</sup> was used, and the total volume sampled was controlled with a calibrated gas meter and a thermometer for temperature compensation. A 142 mm filter (PALL Versapor 1.2 µm) was installed in the probe, but the probe was installed looking away from the gas direction. The justification for this was that particulate buildup on the filter could potentially trap SO<sub>3</sub> onto alumina. On the other hand, omitting filter installation could result in particulate material containing sulfate being included in the analysis and thus constituting a positive error. The "look away" installation of the probe was therefore considered to be the best strategy.

For isopropanol sample bottle method, two (three in the case of using ice) gas washing bottles in plastic material were used in sequence. Isopropyl alcohol (p.a.) was diluted to 80 % vol by de-ionized water. A volume of 400 mL was used in the first bottle. The second (third) bottles were left empty. The bottles were either cooled with cryostat to -20 °C or with water, ice and salt.

For the salt method, about 2 g of NaCl (suprapur) were trapped in a ¾" PFA tube by means of Teflon wool. In order to avoid segregation, the trap was installed in a vertical position. The trap was heated with a jacket to a temperature of about 200 °C in order to avoid condensation of water that could dissolve the salt trap as well as to provide temperature for conversion of the SO<sub>2</sub> to sulfate reactions taking place (Vainio et al., 2013). After samples were returned to the laboratory, they were dissolved in 1.00 L of de-ionized water in a volumetric flask. They were also bubbled with inert gas in order to remove SO<sub>2</sub> that could potentially oxidize to sulfate and interfere with the analytical result.



Figure 1. Sampling on SO<sub>3</sub> onto salt trap. The NaCl trap is shown to the left, and the connected to the sampling probe and with a heating jacket installed in the middle. To the right is shown sampling to two gas washing bottles immersed in a cryostat cooled bath with temperature of -20 °C.

All samples were analyzed by ion chromatography. A Metrohm 883 Basic IC plus with an 858 Professional sample processor was used for analysis. A MetroSep A Supp 5 150/4.0 column were used with a 3.2 mmol/L sodium carbonate, 1.0 mmol/L sodium bicarbonate buffer. A conductivity detector was used. Analysis was

performed as quickly as possible after sampling in order to avoid oxidation of sulfite in the sample. The IC was calibrated with sulfate standards covering the concentration range found in the samples.

The fluoride and sulfate content of the dust collected onto the filters were analysed. For fluoride, a ion-selective electrode was used for analysis (Aarhaug et al., 2012). For sulfate, ion chromatography was used as described earlier in this paper after boiling particulate material in sodium carbonate (10% vol) for 20 minutes.

The SO<sub>2</sub> concentration in the off-gas at GTC3 was estimated with FTIR (ProtIR 204M, 6.4 m path) to be 119 ppm.

## Results

All samples were analysed by ion chromatography. An example of a chromatogram is shown in Figure 2. For sampling in isopropyl alcohol, a sulfite peak was observable in all samples. This implies that even though purging of inert gas was performed before analysis, there are still contributions from SO<sub>2</sub> as sulfite in solution. The contribution from the sulfite already converted to sulfate in the samples at the time of analysis is unknown, but clearly the time between sampling analysis is important. For sampling with salt trap, no sulfite peak was recorded. This suggests that the interference from SO<sub>2</sub> in this method is less of a problem.

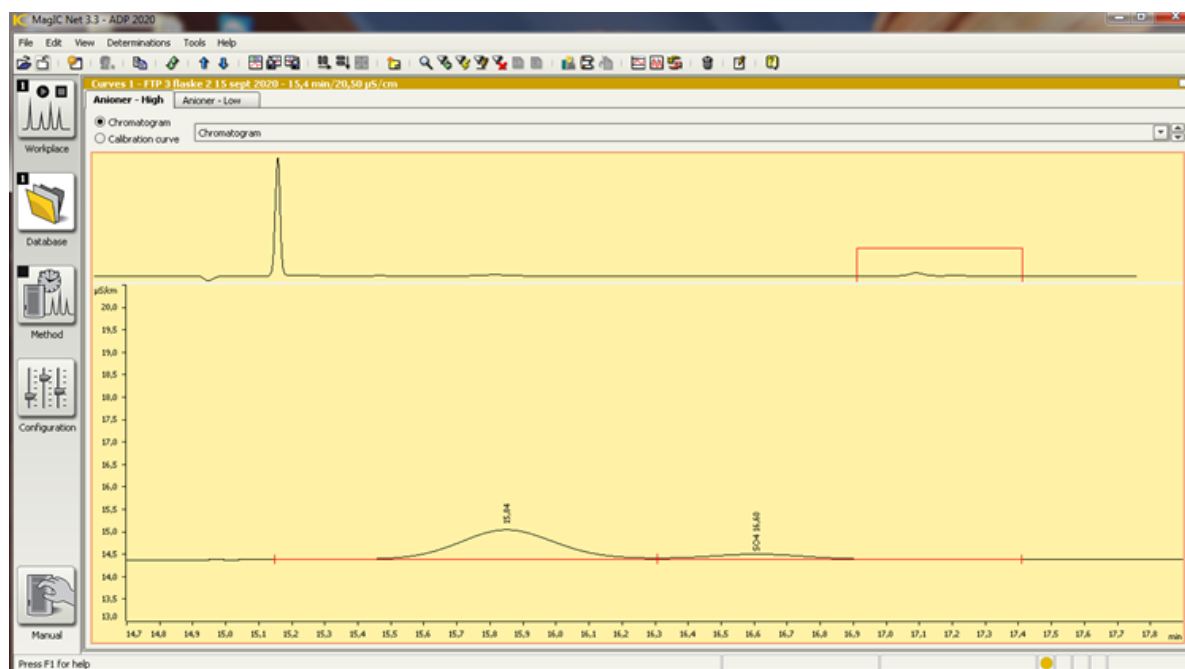


Figure 2. Example ion chromatogram showing sulfite (ret. 15.84 min) and sulfate (ret. 16.60 min). Baseline conductivity was around 14.4 µS/cm.

The results are summarized in Table 1. From GTC3 five samples were collected: two with isopropanol and cryostat cooling, one with isopropanol and ice/salt cooling and one sample onto salt trap. From GTC 1, two samples in isopropanol and cryostat cooling were collected.

For sampling in isopropanol, a significant loss of absorbent from the original 400 mL was observed. Some was recovered in the downstream bottles but overall losses still significant. Comparing ice versus cryostat, the losses were similar even when considering an additional gas washing bottle used in the case of ice/salt. It was also observed that the concentration of sulfate in the bottles were quite similar.

Table 1. Analytical results of ion chromatographic analysis. Volume is the sampled volume of gas corrected for gas meter calibration and corrected for temperature.

Location	Bottle	Cooling	SO <sub>4</sub> (mg/L)	Volume (L)	SO <sub>4</sub> (mg)	Volume (m <sup>3</sup> )	SO <sub>4</sub> (mg/m <sup>3</sup> )	SO <sub>4</sub> (ppm)	mean (ppm)
GTC3	2	Cryo	6.58	0.03	0.16				0.37
	1		8.12	0.33	2.68	1.77	1.60	0.41	
GTC3	2	Cryo	4.32	0.12	0.52				
	1		15.39	0.22	3.38	1.75	2.23	0.57	
GTC3	2	Ice	5.01	0.02	0.10				
	1		7.38	0.30	2.18				
	3		5.92	0.01	0.03	1.81	1.27	0.32	
GTC1	2	Cryo	5.26	0.10	0.53				
	1		6.17	0.26	1.57	1.55	1.36	0.35	
GTC1	2	Cryo	2.90	0.06	0.18				
	1		3.84	0.29	1.11	1.55	0.83	0.21	
GTC3			0.47			0.37	1.28	0.33	
			0.49			0.37	1.32	0.34	

The overall concentration of sulfate in the samples with isopropanol sampling was estimated to be 0.37 ppm. The relative standard deviation is 36 %, partly owing to slightly lower average observed for GTC 1 than GTC 3. No significant difference between using cryostat and ice/salt for cooling was found. For the two parallel analyses of the salt trap sample a value of 0.37 ppm was estimated. The results indicate very good correlation between the two methods and is in support of the fact that any error from dissolved SO<sub>2</sub> in the isopropanol is negligible when analyzing samples almost immediately after sampling.

Taking an average value of 0.35 ppm as the SO<sub>3</sub> concentration found in the off-gas, and assuming a water content of between 1-1.2 % vol, the acid dew point was estimated. Dew point values are plotted in Figure 3. Acid dew point estimation based on (Zarenezhad & Aminian, 2011) plotted by (Solheim, 2022). For the graph, the dew point was estimated to be in the range of 77 to 79 °C.

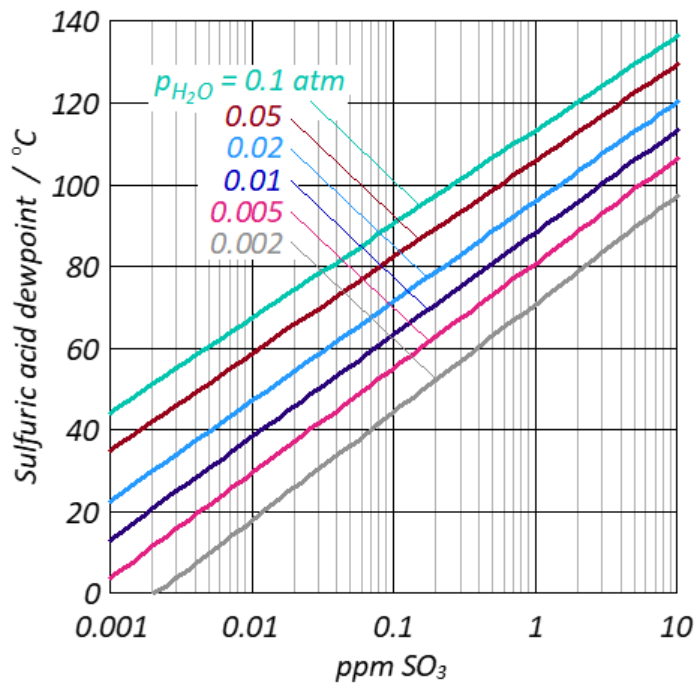


Figure 3. Acid dew point estimation based on (Zarenezhad & Aminian, 2011) plotted by (Solheim, 2022)

The dust collected onto the filter was analyzed for fluoride and sulfate according to standard methodology for the smelter. The fluoride concentration increased with increasing mass of particulate matter. For sulfate, the amount of sulfur did not appear to be a function of mass. The data is shown in Figure 4.

This observation reflects the challenge of sampling of particulate matter while sampling SO<sub>3</sub>: sampling isokinetically would potentially trap SO<sub>3</sub> onto the particulate matter while sampling without a filter could result in contributions from sulfate on alumina in the analysis. The look away probe is a compromise where smaller particulate matter mostly consisting of fluorides (Gaertner et al., 2013) are predominantly collected onto the filter. These fluorides do not exhibit absorption capabilities similar to that of smelter grade alumina for fluoride or sulfur. Therefore, the analysis of the particulate matter shows a mass dependence for fluoride but not for sulfate that is not trapped onto the fluoride particles.

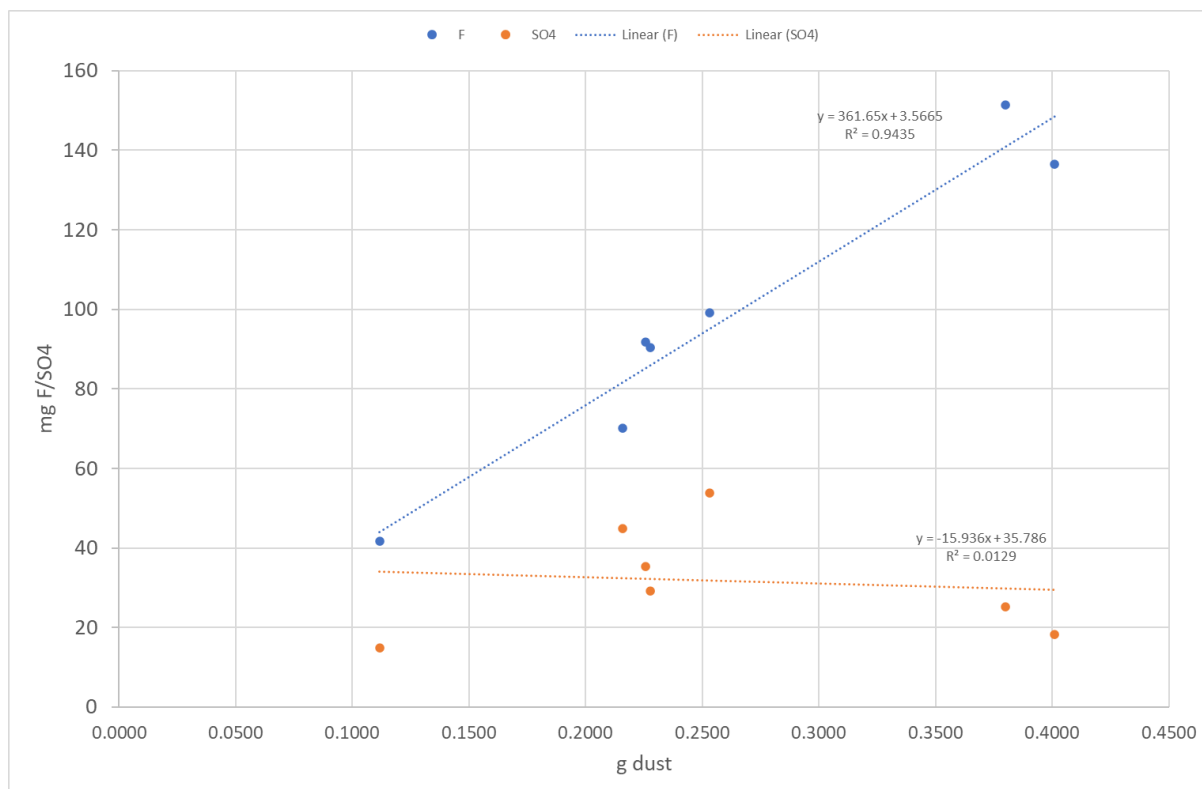


Figure 4. Collected particulate matter analyzed for fluoride and sulfate.

## Discussion

Two methods for assessment of acid dew point in off-gas from primary aluminium production has been evaluated. The methods give fairly similar results, with an average of 0.35 ppm. Assuming a water content of 1-1.2 % vol in the gas, this translates to an acid dew point temperature between 77 to 79 °C. The salt trap sampling methods was found easy to conduct. For sampling in 80 % vol isopropanol, some oxidation of SO<sub>2</sub> to sulfate seem to be difficult to avoid unless immediate analysis of the samples is performed. This despite purging of the sample with inert gas. Nevertheless, the two methods compared are in very good agreement, suggesting that immediate analysis of isopropanol after sampling minimizes the problem of having contributions to the sulfate concentration from dissolved SO<sub>2</sub> being oxidized in the solution.

When the SO<sub>3</sub> concentration value of 0.35 ppm is compared to the measured value of SO<sub>2</sub> in the off-gas of 119 ppm, this means that the conversion of SO<sub>2</sub> to SO<sub>3</sub> is less than 0.3 %. This is much lower than the value of between 1 and 5 % often assumed.

Sampling was not performed isokinetically, but using a look-away orientation of the probe. This was done to avoid SO<sub>3</sub> to the particulate matter collected onto the filter. Analysis of the particulate matter indicates that the sulfate concentration is not a function of the particulate mass. This indicates that sulfates are not trapped by the filter and thus affecting the sulfate concentration and acid dew point estimate. Further work should be performed in order to find a good strategy for sampling SO<sub>3</sub> in the presence of particulate matter.

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