Chemical pulping

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Method for analysis of ClO_2 and Cl_2 air emissions from pulp mill

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Abstract: Chlorine dioxide is commonly used as a bleaching agent in kraft pulp mills. Scrubbers are required to remove any remaining ClO_2 from the plant tail gases. To control the air emissions of chlorine compounds, chlorine dioxide and chlorine contents must be monitored to ensure that the strict regulatory standards are met. However, the currently used analytical method is not suitable for detection of low concentrations of chlorine and chlorine dioxide. A new method for measuring chlorine dioxide and chlorine emissions was developed, which ensures compliance with the stringent requirements imposed by the authorities. The two species could be measured separately with a limit of quantification of 3 ppm. The method was robust and easy to use in the pulp mill environment and it was validated both in the laboratory and the field. The specificity of the method was demonstrated, Cl_2 analysis was not sensitive to the presence of ClO_2 and vice versa. The uncertainty ($\pm 2 \times \text{RSD}$) of the analytical method in the field was estimated from duplicate measurements performed in the range of 3–500 ppm for ClO_2 and 3–300 ppm for Cl_2 , and was found to be $\pm 20\%$ and $\pm 10\%$, respectively. Possible interferences in the analytical method are also discussed.

Keywords: analytical method; bleaching; chlorine; chlorine dioxide; emissions; field study; pulp mill.

Introduction

Environmentally friendly elemental chlorine-free (ECF) bleaching of kraft pulp is the most commonly used pulp bleaching process worldwide and is currently regarded as Best Available Technique (Suhr et al. 2015). The active agent in ECF bleaching is chlorine dioxide, ClO_2 , which is inherently unstable and must be produced at the pulp mill for safety reasons (Vogt et al. 2010). In order to comply with ClO_2 air emission regulations, a scrubber is usually used for its removal from the effluent gas stream. Pulp mills are obliged to monitor the atmospheric emissions of chlorine compounds by measuring the emissions of chlorine dioxide and chlorine. Although regulations vary worldwide with large local differences, there is a global trend towards lowering the maximum permitted emission levels. In Europe, a new reference document regulating pollutant emissions from industrial installations is under preparation (WGC BREF, Common Waste Gas Treatment in the Chemical Sector; in preparation by European Commission). Currently, the most widely used analytical method for measuring chlorine and chlorine dioxide in off-gases at pulp mills is a dual-pH potassium iodide method using an impinger system (Stryker 1997, Fisher et al. 1987). In this dual-pH titration method, the sample is collected by pumping the emission gas through two impingers containing a buffered neutral potassium iodide solution, where the following reactions take place:

After sampling, the formed iodine is titrated with thiosulfate. The solution is then acidified, and the following overall reaction takes place:

The acidified solution is titrated with thiosulfate, and the chlorine dioxide and chlorine concentrations are calculated. This type of titration method distinguishing between chlorine dioxide and chlorine has also been used for aqueous samples (Franson 1998, Aieta et al. 1984). However, this method suffers from several drawbacks, which

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makes it unsuitable for the analysis of very low concentrations (<20 ppm) found in emissions to air from modern pulp mills. The dual-pH titration is sensitive to any deviation from the optimum pH of the buffered KI solution, with too high or too low pH values leading to underestimation or overestimation of the chlorine concentration, respectively (Fisher et al. 1987). Another inherent drawback of the method is the significant increase in analytical error with increasing difference in the concentrations of the two analytes, which are calculated by subtracting the data obtained in the two titration steps (Stryker 1997). Moreover, the limit of quantification of this method is not specified in the literature, and the precision is reported for a concentration range significantly higher than the permitted emission limits many pulp mills are obliged to follow.

Hence, a more robust, validated analytical method that would ensure compliance with the stringent requirements imposed by the authorities is highly desirable. The method must be able to separate chlorine dioxide and chlorine, with a limit of quantification of 5 ppm or less for both compounds, and must be applicable to the manufacturing environment of pulp mills where the measurement is performed. In this study, a new method that fulfills these requirements and does not suffer from the drawbacks of two-step titrations was developed, in which chlorine and chlorine dioxide were analyzed separately. No interference between chlorine and chlorine dioxide was observed, and the accuracy of the method was therefore not affected by the difference in the concentration of analytes. The proposed analytical method was validated both in the laboratory and the field to determine the uncertainty components of the method and verify its robustness in the field.

Materials and methods

Description of the analytical method

The method (Appendix A) consists of a sampling and an analytical procedure. For sampling, the equipment shown in Figure 1 was used to determine the volume of the sampled gas with high precision. The gas flow rate through the system should be 5–120 l/h, and the recommended rate is 90 l/h. To achieve high accuracy at low concentrations, a minimum of 150 l gas is needed.

The first impinger contains the emission solution consisting of 2 g/l sodium hydroxide and 2 g/l hydrogen peroxide. The second impinger contains a buffered potassium iodide solution (10 % KI), which becomes colored if ClO₂ or

Figure 1: Scheme of the sampling setup.

Cl₂ enters the second impinger during sampling, thus indicating that the sampling procedure has failed. When the gas is entering the first impinger it is captured in the emission solution by the following reactions (Connick 1947, Flis et al. 1957, Gordon et al. 1972, Kumar and McCluskey 1987, Wang and Margerum 1994):

Chlorine dioxide and chlorine are determined by analyzing the chlorite and chloride content of the emission solution, respectively.

The titrations can be performed directly after sampling or the emission solution can be stored up to two weeks at room temperature before analysis.

The chlorite content is determined by acid thiosulfate titration (Kolthoff et al. 1957). Prior to titration, the excess hydrogen peroxide is destroyed by addition of catalase (Northrop 1925, Keilin and Hartree 1938).

Chlorite is reduced by reaction with iodide in acidic solution (Kolthoff et al. 1957):

The iodine is then determined by thiosulfate titration:

The chloride content of the emission solution is determined by potentiometric titration based on the addition of silver nitrate and a silver electrode for the determination of the equivalence point (Jefferey et al. 1989). The concentrations in ppm in the sampled gas volume is calculated using the titration results and the total gas volume, see Appendix A.

Validation in the laboratory

The specificity, accuracy, and repeatability of the two titration steps were evaluated separately. Standard solutions of

Table 1: Approximate concentrations of ClO₂ and Cl₂ in the four test solutions A–D. All solutions contained 2 g/l NaOH and 2 g/l H₂O₂.

Test solution	ClO ₂ (g/l)	Cl ₂ (g/l)
A	0.1	0
B	0	0.1
C	0.1	0.1
D	0.02	0.02

chlorine and chlorine dioxide were used to prepare samples with different compositions (Table 1).

Preparation of the ClO₂ standard solution

A standard acidic, chlorine-free ClO₂ solution was prepared from an acidic solution (adjusted to pH 1.5 with H₂SO₄, Scharlau, Reagent grade) of 50 g/l NaClO₂ (Sigma Aldrich, PA) placed in an impinger bottle. Two more impingers containing acidified Milli-Q (MQ) water (adjusted to pH 2.5 with H₂SO₄) were placed in series, and ClO₂ was passed from the first to the second bottle under pressure using a water filter pump. After ~30 min, the ClO₂ concentration in the second bottle was ~3 g/l. The exact ClO₂ concentration was determined by a manual acid thio-sulfate titration (Franson 1998) using KI (Scharlau, ACS), 2.5 M H₂SO₄ (Scharlau), and a dilute, standardized 0.05 M Na₂S₂O₃ solution (Merck, TitriPUR®).

Preparation of the Cl₂ standard solution

A standard acidic, chlorine dioxide-free Cl₂ solution was prepared from an acidic NaClO solution (Borregaard, specification BRGQMS-71131, ~150 g/l adjusted to pH < 2 with H₂SO₄) placed in an impinger bottle. Two more impingers

containing MQ water were placed in series, and Cl₂ gas was passed from the first to the second bottle under pressure using a water filter pump. After ~30 min, the Cl₂ concentration in the second bottle was ~2 g/l. The exact Cl₂ concentration was determined by a manual arsenite titration (Kolthoff et al. 1957) using a 10 % NaOH solution prepared from Eka NaOH pellets, NaHCO₃ (Riedel-de Haën, for analysis, ACS), KI (Scharlau, ACS), and a 0.05 M NaAsO₂ solution (Honeywell, Fluka™) diluted to 0.025 M.

Sample compositions

When the analytical method was applied in the field, typical concentrations of ClO₂ and Cl₂ in the emission solution after gas absorption were between 0.02 g/l and 0.2 g/l each. Four different test solutions (A–D) were prepared from the standard ClO₂ and Cl₂ solutions, and their compositions are shown in Table 1. The concentrations of Cl₂ and ClO₂ were chosen in such a way that the repeatability was estimated at LoQ and in the middle of the measuring range. The repeatability is expected to be similar in the middle and the upper part of the measuring range, while it is expected to be higher close to LoQ.

The NaOH used were Eka NaOH pellets and the H₂O₂ used was Eka HP C59.

To verify the accuracy of the method, the exact nominal concentrations of the test solutions were calculated based on added amount of standard solution and compared with the analytical results (Table 2).

Analysis

In the laboratory study, ClO₂ determination was performed as described in Appendix A. The following chemicals were used: NaHCO₃ for analysis (ACS Reagent, Riedel-de

Table 2: Nominal and analytical ClO₂ and Cl₂ concentrations of emission solutions A–D.

Test solution	A – ClO ₂	B – Cl ₂	C – Both high	D – Both low
Nominal ClO ₂ (g/l)	0.138	0	0.183	0.0178
Nominal Cl ₂ (g/l)	0	0.089	0.132	0.0198
Analytical results				
ClO ₂ mean (g/l)	0.134	<0.002	0.178	0.0189
ClO ₂ spread (2×RSD%)	n. a.	n. a.	2.3	3.6
Yield (%)	97	n. a.	97	106
Number of titrations	2	2	10	10
Cl ₂ mean (g/l)	<0.001	0.0923	0.132	0.020
Cl ₂ spread (2×RSD%)	n. a.	n. a.	2.9	4.4
Yield (%)	n. a.	104	100	101
Number of titrations	2	2	10	10

Haën), catalase from *micrococcus lysodeikticus* (Fluka), Quantofix[®] Peroxide 100 (Macherey-Nagel), 2.5 M H₂SO₄ (Scharlau), KI (ACS reagent, Scharlau), and 0.1 M Na₂S₂O₃ (diluted to 0.05 M) (TitriPUR[®], Merck).

Cl₂ analysis was also performed according to the method described in Appendix A. For the automatic titration, a Titrand 888 automatic titrator (Metrohm) equipped with a Ag-titrode 6.0430.100, a sample exchanger (814 USB Sample Exchanger), and the Tiamo software (v 2.5) were used. The chemicals used were 2.5 M H₂SO₄ (Scharlau) and 0.1 M AgNO₃ (diluted to 0.01 M) (Scharlau).

Stability test of H₂O₂ in the emission solution

To ensure that an excess of hydrogen peroxide is present during the entire sampling period, the stability of hydrogen peroxide in the emission solution was investigated in a separate test. Emission solutions with the same NaOH and H₂O₂ concentrations used in the analysis (Appendix A) were prepared. The NaOH used were Eka NaOH pellets and the H₂O₂ used was Eka HP C59. In addition, DI water was used. The H₂O₂ concentration was analyzed by the Perex Test[®] [1.16206 Merck].

Validation at the pulp mill

In the validation of an analytical method, the complexity of sampling is an important factor contributing to the uncertainty of the measurements. In the laboratory study, it was not possible to include the in field sampling procedure. Instead, it was covered in the validation at the pulp mill.

Repeated field measurements of ClO₂ and Cl₂ in the emission gas can vary due to process variations over time. To avoid this problem, parallel analyses were performed using two series of impinger bottles for simultaneous sampling. The estimation of the repeatability based on duplicates described in the Eurachem/Citac Guide CG4 (Ellison and Williams 2012) was used to estimate the method uncertainty at different concentrations of ClO₂ and Cl₂.

For the determination of the limit of quantification (LoQ), repeated measurements at low concentrations close to the LoQ are necessary. Thus, several measurements were performed at low Cl₂ and ClO₂ concentrations, i. e. using a sampling point after the chemical scrubber. However, these data may be associated with process variations, suggesting that the LoQ could be even lower. The obtained

standard deviation (σ) was used to estimate the LoQ by Equation 9 (Lloyd 1995):

$$\text{LoQ} = 10 \times \sigma \quad (9)$$

This is a well-established practice in analytical chemistry, and it suggests that 10 % relative standard deviation (RSD) is acceptably close to the LoQ. For a better understanding of the uncertainty components of the method, uncertainty estimates were calculated for the different steps and combined with propagation (Ellison and Williams 2012). The combined uncertainty was compared with the uncertainty based on the duplicate data obtained from the parallel measurements at the pulp mill.

Results and discussion

Validation in the laboratory

The method was first validated in the laboratory, and the Cl₂ and ClO₂ concentrations of solutions A–D obtained using the proposed analytical method are shown in Table 2 together with the corresponding nominal values.

The accuracy of the method for the determination of ClO₂ and Cl₂ was evaluated from the calculated yield. The highest deviation from the nominal value was found for the ClO₂ concentration in test solution D, with a yield of 106 %. This was considered an acceptable deviation considering the small losses due to volatile components, which can affect several steps in the validation process, namely, the titration of the standard solution, preparation of the test solutions, and final analysis. These small errors can accumulate and affect the final yield calculation. However, this deviation was insignificant compared to the overall performance and uncertainty of the method.

In all cases, the spread of repeated measurements, expressed as two times the relative standard deviation (2×RSD), was <5 %. In the titration step of the Cl₂ analysis, such a low spread was obtained when about 2 ml or more of AgNO₃ were used, whereas with AgNO₃ amounts <1 ml, the spread was more than doubled. The choice of titration parameters in the automatic titrator (Appendix A) was fundamental for good repeatability, especially when small volumes of AgNO₃ were consumed.

Notably, Cl₂ was not affected by the presence of ClO₂ and vice versa, demonstrating the good specificity of the method.

To determine the gas absorption efficiency of the analytical method, the sensitivity for color change in the safety

impinger bottle containing buffered KI solution (Figure 1) was evaluated. Low amounts of Cl_2 and ClO_2 were added separately using the prepared standard solutions. For both Cl_2 and ClO_2 , a clear color change of the buffered KI solution was observed at a concentration of 0.01 mg/l.

During field measurements, no color change in the safety impinger was observed, hence an absorption efficiency higher than 99.5 % was verified.

Stability of H_2O_2 in the emission solution

During sampling, an excess of hydrogen peroxide in the emission solution is required (Equation 4 and Equation 6). Hence, a H_2O_2 amount about four times the upper measurement limit (500 ppm ClO_2) is used. To ensure that an excess of hydrogen peroxide is present during the entire sampling period, the stability of hydrogen peroxide in the emission solution was investigated.

Figure 2: H_2O_2 concentration in the emission solution versus time at 25 °C.

The stability test shows that the hydrogen peroxide concentration is stable for at least 2 days and then it starts to decompose slowly (Figure 2) with a half-life time of 5 days. This suggests that the use of high-quality chemicals and water for the preparation of the emission solution allowed preservation of the excess hydrogen peroxide during the sampling procedure. Nevertheless, hydrogen peroxide test sticks (Quantofix Peroxide 25) can be used to confirm that excess hydrogen peroxide is still present in the emissions solution after sampling.

Validation at pulp mill

To include all factors contributing to the overall uncertainty, the analytical method was also validated at the

pulp mills. Emission measurements were performed in 14 different occasions at ClO_2 plants in four different pulp mills, according to the method described in Appendix A. The measuring points varied depending on the type and design of the ClO_2 plant, and included the absorption tower, ventilation scrubber, chemical scrubber, and bleachery scrubber.

The precision of the method was investigated by setting up two equal sampling equipments in parallel at the pulp mill. With this approach, the estimation of the repeatability based on duplicates can be taken as the overall uncertainty of the analytical method. However, the systematic error shall also be included but the observed bias in the laboratory study was small enough to be neglected in the overall uncertainty.

Chlorine dioxide – LoQ and uncertainty of the analysis

Based on repeated measurements of ClO_2 at low concentrations, the LoQ was determined to be 3 ppm.

The uncertainty, expressed as $\pm 2 \times \text{RSD}\%$, was estimated to be $\pm 20\%$ at low ClO_2 concentrations (3–25 ppm) and $\pm 15\%$ at ClO_2 concentrations in the range of 25–500 ppm, based on field measurements (duplicate sampling) (Figure 3). This is in line with the performance of the analytical method expected for ppm levels and with the Horwitz equation, which expresses the uncertainty as a function of the measured concentration (Gustavo González and Ángeles Herrador 2007). The validated range was 3–500 ppm ClO_2 . In addition, concentrations as low as 0.5–3 ppm could be detected but the uncertainty can be up to $\pm 50\%$.

Figure 3: Uncertainty of ClO_2 analysis calculated as $2 \times \text{RSD}\%$ versus the concentration in the off-gas. Concentration ranges are presented. For each concentration interval, the number of duplicate samples is shown in the bars.

Figure 4: Uncertainty of Cl₂ analysis calculated as 2×RSD% versus the concentration in the off-gas. Concentration ranges are presented. For each concentration interval, the number of duplicate samples is shown in the bars.

Chlorine – LoQ and uncertainty of the analysis

Based on repeated measurements of Cl₂ at low concentrations the LoQ was determined to be 3 ppm. The uncertainty, expressed as ±2×RSD%, was estimated to be ±10 % in the validated concentration range of 3–300 ppm Cl₂, based on field measurements (duplicate sampling) (Figure 4). In addition, concentrations as low as 0.5–3 ppm could be detected but the uncertainty can be up to ±50 %.

Stability of the emission solution after sampling

The stability of the emission solution after sampling determines the time between sampling and titration. The concentration of sodium chlorite and sodium chloride in the emission solution after sampling versus time was determined (Table 3). Clearly, the change in concentration with time did not exceed 4 %, remaining within the uncertainty of the titration step (±5 %). This result demonstrates that,

Table 3: Stability test: concentration of sodium chlorite and sodium chloride in the emission solution versus time.

Test #	Component	0 day (mg/l)	7 days (mg/l)	48 days (mg/l)	98 days (mg/l)
1	NaClO ₂	0.224	0.225		
2	NaClO ₂	0.117			0.114
		0.118			0.120
3	NaCl	0.040	0.038		
		0.040	0.039		
4	NaCl	0.090		0.093	
		0.109		0.110	

after sampling, the emission solution was very stable. Notably, the use of dark bottles did not improve the stability.

The high stability of the emission solution suggests that sampling and analysis can be performed in different days. This is a great advantage of the analytical method, as it allows sending samples for analysis to a laboratory, avoiding the transfer of the complex equipment to the ClO₂ plants, thus demonstrating the robustness of the method.

Uncertainty components of the analytical method

In order to compare the spread in analytical data between laboratory and field studies, other uncertainty components were considered.

The final concentration of both ClO₂ and Cl₂ in the gas was determined from the volume of gas passing through the impinger bottle, the volume of liquid in the impinger, and the volume of titer consumed (0.01 M AgNO₃ and 0.05 M Na₂S₂O₃, respectively). The sampled gas volume depends on the following four parameters (Equation A.3 in Appendix A):

- atmospheric pressure,
- temperature,
- gas flow rate,
- gas sampling time.

The uncertainty in gas volume was obtained by propagation of the estimated uncertainties of these variables. Because atmospheric pressure was not measured, natural variations must be accounted for and were set to ±5 %. The uncertainties of temperature, gas flow rate, sampling time, and liquid volume were set based on the accuracy of the field measurements. The uncertainty of titration volumes observed in the laboratory study was used for the estimation of a total combined uncertainty of the analytical method, i. e., final ClO₂/Cl₂, as shown in Table 4.

The overall uncertainty of the analytical method estimated from propagation of the different uncertainty components was ±8 % for both ClO₂ and Cl₂ analyses. This value was compared with the uncertainty obtained from the validation at the pulp mill, i. e., parallel duplicate measurements (Figures 3 and 4). The only major difference was that the pulp mill uncertainty estimation was higher for ClO₂, especially at low concentrations. The reason for this could be that the chlorine dioxide determination procedure included more manual steps compared to chlorine determination. This affected the uncertainty of the field measurements where different operators were

Table 4: Estimates of uncertainty components and propagated total uncertainty for ClO₂ and Cl₂ determination.

Parameter	Unit	Typical value	Uncertainty (absolute)	Uncertainty (relative, %)
Atmospheric pressure	Atm	1	0.05	5
Temperature	K	288	1	0.3
Gas flow rate	ml/min	1500	50	3
Sampling time	min	60	1	2
Gas volume	Nm ³	0.085	0.005 ^a	6 ^a
Liquid volume in flask	ml	100	1	1
Titer volume Na ₂ S ₂ O ₃	ml	0.5	0.025	4 [*]
Titer volume AgNO ₃	ml	2	0.1	5 [*]
Total uncertainty of the analytical method				
ClO ₂	ppm	3.6	0.29 ^a	8 ^a
Cl ₂	ppm	5.7	0.46 ^a	8 ^a

^a, propagated value obtained from uncertainties of the other parameters; ^{*}, ±2×RSD of the laboratory study.

involved and the conditions were not optimal for laboratory analysis. Nevertheless, the uncertainty and LoQ of the method fulfill the requirements, demonstrating a significant improvement compared to previous methods.

Robustness and interferences

Possible interferences in this analytical method are gaseous or aerosol species reactive toward chlorine, chlorine dioxide, chlorite, chloride, and hydrogen peroxide, or capable of oxidizing iodide in the titration step. Substances that deactivate catalase also interfere with the analysis because the residual hydrogen peroxide in the titration step would give a false (too high) result in the chlorine dioxide analysis. Moreover, chemicals reacting with chlorite/chlorine dioxide often produce chlorides, leading to too-low and too-high results in chlorine dioxide and chlorine analyses, respectively, and compounds reacting with chloride would give a false (too low) result in the chlorine measurement.

Chemicals typically present at pulp mills, such as hydrogen peroxide, ozone, sulfur dioxide, sulfite, hydrogen sulfide, and volatile organic acids, can interfere with the analysis. To avoid possible interferences, it is important to select sampling points within the chimney where there is no back-mixing of airborne chemicals from the environment. However, even if sampling is performed correctly, aerosols and gaseous species from the scrubber, e.g., aerosol sulfite or sulfur dioxide released by a too acidic bisulfite scrubber solution, can interfere with the analysis.

Aerosols interferences can be avoided by using an aerosol trap (e.g., an empty impinger bottle) before the impingers.

The previously reported dual-pH potassium iodide method suffers from the same interferences and is also affected by the presence of hydrogen peroxide.

The robustness of the new method stems from the stability of the sample, which can be sent to an analytical laboratory for titration in case of limited possibilities at the pulp mill. In addition, unlike the previous method, the new method is not sensitive to slight variations of pH or composition of the emission solution. Due to the high pH of the emission solution in the new method, reaction 4 and 5 are strongly shifted to the right hence a minor pH difference does not have a significant impact (Connick 1947, Flis et al. 1957, Gordon et al. 1972, Kumar and McCluskey 1987, Wang and Margerum 1994):

Cl₂ analysis was not sensitive to the presence of ClO₂ and vice versa, demonstrating the specificity of the method. Moreover, the accuracy of the analysis of an analyte was independent of the concentration range of the other. All these properties make the new method robust and easy to use at pulp mills with limited access to laboratory facilities.

Conclusions

A new method for the determination of chlorine dioxide and chlorine emissions was developed, which could be used for measuring the two species separately with good reproducibility and a limit of quantification of 3 ppm. The method was robust and easy to use at remote pulp mills.

The analytical method was validated both in the laboratory and in the field. Notably, Cl₂ analysis was not sensitive to the presence of ClO₂ and vice versa, demonstrating the specificity of the method.

Table 5: Summary of method performance. The uncertainty is expressed with a 95 % confidence interval (2×RSD).

Analyte	LoQ	Measurement range	Uncertainty
ClO ₂	3 ppm (*)	3–25 ppm	±20 %
ClO ₂		25–500 ppm	±15 %
Cl ₂	3 ppm (*)	3–500 ppm	±10 %

For both ClO₂ and Cl₂, 0.5–3 ppm can be detected but the uncertainty can be up to ±50 %.

The remarkable performance, summarized in *Table 5*, reveals that the current stringent requirements on chlorine and chlorine dioxide levels in air emissions from pulp mills were met.

Conflict of interest: The authors declare no conflicts of interest.

Appendix A

Sampling procedure

The sample point can be a drilled hole of about 8 mm in the chimney of the absorber, vent scrubber, or chemical scrubber. The equipment consists of two impinger bottles of ~200 ml with a distributor, minimum P2, a pump providing a constant flow rate between 5 l/h and 120 l/h (recommended flow: 90 l/h), and a gas flow meter (rotameter) (with an accuracy of ±50 ml/min). The equipment is set up according to Figure 1. If the off-gas contains large amounts of moisture, an empty impinger serving as a moisture trap can be added before the impinger containing the emission solution. Add about 110 ml of the emission solution (2 g/l NaOH PA grade and 2 g/l H₂O₂, chemical grade) into impinger 1. The bubble height must be at least 10 cm. The off-gas is bubbled through the system with a constant flow rate, ensure no carry-over of the emission solution due to the high flow rate. Use a second impinger (2) containing ~100 ml buffered KI solution (100 g/l KI reagent grade +5 g/l NaHCO₃ PA grade +32 g/l K₂HPO₄ PA grade) to verify that no Cl₂ or ClO₂ is passing through the first impinger during sampling. If Cl₂ or ClO₂ enters the second impinger the KI solution gets colored, indicating that the sampling procedure failed. If sampling has failed, try to use shorter sampling time, and/or lower flow rate, check the bubbling height in impinger 1 and check the gas distributor to ensure small bubbles. For an accurate detection of low concentrations close to the LoQ, a minimum of 150 normal liter gas, has to be pumped through the impinger. Measure the

temperature after the flowmeter, note the measuring time, the flow rate and measure the volume of emission solution in the impinger.

Analysis of chlorine dioxide

Take 50.0 ml of the emission solution into a beaker while stirring. The presence of H₂O₂ in the emission solution can be tested using HP sticks. Add 1–2 g NaHCO₃ (s) (PA grade) and check that pH is between 7 and 9. Add One drop of catalase suspension and wait for 5 min. Check H₂O₂ content with a HP sticks: if the H₂O₂ concentration is ≤0.3 mg/l proceed, but if not, add one more drop of catalase and wait 5 min to check again. Add Sulfuric acid (2M) (PA grade) cautiously until pH < 2, and then add 20 ml of 10 % KI (reagent grade). Titrate potentiometric or manually using 0.050 M Na₂S₂O₃ (PA grade), and note the amount as A ml. For high accuracy, a minimum volume of 0.5 ml is needed and for manual titration, starch provides a better identification of the equivalence point.

Analysis of chlorine

Take 50.0 ml of the emission solution into a beaker while stirring and add 5 ml sulfuric acid (2M) (PA grade). Perform a potentiometric titration where 0.010 M AgNO₃ (PA grade) is added and a silver electrode is used for the determination of the equivalence point. As a guideline, the setting in the automatic titrator shall ensure a minimum equilibration time of 80 s and the maximum signal drift of 8 mV/min. Note the volume of AgNO₃ as B ml. For high accuracy, a minimum volume of 2.0 ml is needed.

Calculations

Chlorine dioxide content of the emission solution:

$$\text{ClO}_2 \text{ content (mg)} = \frac{A * C * M_w * V_{\text{tot}}}{E * V_s} \quad (\text{A.1})$$

where A (ml) is the volume of Na₂S₂O₃, C (M) the concentration of Na₂S₂O₃, M_w (g/mole) the molecular weight of ClO₂, V_{tot} (ml) the total volume of emission solution, E the equimolar factor for the thiosulfate (=4), and V_s (ml) is the sample volume.

Chlorine content of the emission solution:

$$\text{Cl}_2 \text{ content (mg)} = \frac{B * C * M_w * V_{\text{tot}}}{E * V_s} \quad (\text{A.2})$$

where B (ml) is the volume of AgNO₃, C (M) the concentration of AgNO₃, M_w (g/mole) the molecular weight of Cl₂, V_{tot} (ml) the total volume of emission solution, E the equimolar factor for the silver nitrate (=2) and V_s (ml) is the sample volume.

Sampled gas volume:

$$SV_{\text{gas}} (\text{Nm}^3) = \frac{Q * P * T_{\text{ref}} * t}{1000 * (T_{\text{ref}} + T) * 60} \quad (\text{A.3})$$

where Q (l/h) is the measured gas flow through the impinge, P the pressure after flowmeter (=1 atm), T_{ref}, the reference temperature (273 K), t (minutes) the measuring time and T (°C) is the gas temperature measured after flow meter.

ClO₂ emission:

$$\text{ClO}_2 \text{ emission } (\text{mg/Nm}^3) = \frac{\text{ClO}_2 \text{ content}}{SV_{\text{gas}}} \quad (\text{A.4})$$

$$\text{ClO}_2 \text{ emission (ppm)} = \frac{\text{Emission ClO}_2 * 24.4}{67.45} \quad (\text{A.5})$$

where 67.45 g/mole is the molecular weight of chlorine dioxide, and 24.4 l/moles is the volume of 1 mole of ideal gas (25 °C).

Cl₂ emission:

$$\text{Cl}_2 \text{ emission } (\text{mg/Nm}^3) = \frac{\text{Cl}_2 \text{ content}}{SV_{\text{gas}}} \quad (\text{A.6})$$

$$\text{Cl}_2 \text{ emission (ppm)} = \frac{\text{Emission Cl}_2 * 24.4}{71} \quad (\text{A.7})$$

where 71 g/mole is the molecular weight of chlorine.

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