



Lappeenranta-Lahti University of Technology LUT
School of Energy Systems
Electrical Engineering
Master's Thesis
2019

Janne Jäppinen

MEASUREMENT OF GAS CONCENTRATIONS IN AN ENVIRONMENTAL MIXED FLOWING GAS TEST CHAMBER

Examiners: Professor Pertti Silventoinen
D.Sc Tommi Kärkkäinen

"Assumption is the mother of all fuck-ups"
Marcus Penn in Under Siege 2: Dark Territory (1995) directed by Geoff Murphy

Abstract

Janne Jäppinen

Measurement of gas concentrations in an environmental mixed flowing gas test chamber

Master's Thesis

Lappeenranta 2019

38 pages

Examiners: Professor Pertti Silventoinen
D.Sc Tommi Kärkkäinen

Keywords: mixed flowing gas, gas concentration measurement, uncertainty analysis

Durability of industrial electronic components and systems can be tested with mixed flowing gas (MFG) tests. In mixed flowing gas tests electronics are exposed to parts-per-billion trace level pollutant gases in a test chamber and their effects on the devices are assessed. The test conditions consists of controlled temperature, humidity and pollutant gases. To assure correct test conditions the gas concentrations have to be measured with accuracy. In this thesis different measurement methods for the pollutant gases are presented and the most suitable ones are chosen for MFG use.

Industry standards on MFG tests list many different measurement methods for gas concentration analysis. Their advantages and disadvantages are assessed and uncertainty analysis is done for the most suitable analyzers of these measurement methods. For sulfur dioxide and hydrogen sulfide the most suitable method is ultraviolet fluorescence spectroscopy. For nitrogen dioxide the most suitable methods are chemiluminescence and cavity attenuated phase shift spectroscopy. With chlorine a colorimetry-based chemcassette method is deemed the most suitable with caveats.

Main source of uncertainty for the analyzers is identified as the one caused by linearity. For most analyzers the uncertainty of linearity can be brought down by calibrating the device to a lower gas detecting range. Outside of uncertainty analysis an effect of humidity on measurement was found in ultraviolet fluorescence spectroscopy and chemiluminescence. This effect has to be characterized before conducting MFG tests.

Tiivistelmä

Janne Jäppinen

Kaasujen konsentraation mittaus virtaavassa monikaasu ympäristötestauksessa

Diplomityö

Lappeenranta 2019

38 sivua

Työn tarkastajat: Professori Pertti Silventoinen
 Tkt Tommi Kärkkäinen

avainsanat: monikaasu ympäristötestaus, kaasun konsentraation mittaus, epävarmuustarkastelu

Teollisen elektroniikan toimintavarmuutta voidaan testata virtaavalla monikaasu ympäristötestillä. Monikaasu ympäristötestauksessa elektroniikkaa altistetaan miljardisosan jäämätason kaasukonsentraatiolle testauskammiossa ja kaasujen vaikutus laitteisiin arvioidaan. Testiympäristön lämpötilaa, ilmankosteutta ja kaasujen konsentraatiota valvotaan. Jotta oikeisiin testiolosuhteisiin päästään, on kaasujen konsentraation mittaukseen käytettävä erityistä huolta. Tässä diplomityössä eri kaasunmittaustapoja esitellään ja sopivimmat valitaan jatkokäyttöön.

Monikaasutestejä koskevat standardit listaavat monia eri mittausmenetelmiä kaasujen konsentraation selvittämiseksi. Eri menetelmien soveltuvuutta arvioidaan ja epävarmuustarkastelu tehdään kaikista sopivimmille analyyseille tämän arvion pohjalta. Rikkidioksidin ja rikkivedyn mittaamiseen sopivin menetelmä on ultravioletti fluoresenssispektroskopia. Typpidioksidin mittaamiseen parhaiten soveltuu kemiluminesenssin menetelmä sekä kavitteettiavusteinenvaihe-erospektroskopia. Kloorille taas soveltuu parhaiten kolorimetrisen chemcassette-menetelmä tietyin varauksin.

Epävarmuuden päälähde eri analyyseille tunnustettiin linearisuuden aiheuttamaksi. Useimmilla arvioiduilla analyyseillä lineaarisuuden aiheuttama epävarmuutta voi laskea kalibroimalla mittalaite matalemmalle mittausalueelle. Epävarmuustarkastelun ohessa löytyi myös ilmankosteuden aiheuttama vaikutus mittauksiin ultravioletti fluoresenssispektroskopiassa ja kemiluminesenssissa. Tämä vaikutus tulee luonnehtia ennen monikaasutestien tekemistä.

Preface

This thesis was written in the laboratory of Applied Electronics of LUT University in 2019. The thesis is done for the ABB/LUT collaborative research project Chemical Exposure and Corrosion of Electronics. I would like to thank ABB for funding and for bringing this important research topic to my attention.

From LUT University I would like to thank Professor Pertti Silventoinen and Dr. Tommi Kärkkäinen for their supervision of my thesis and guidance to the world of academic research.

A big thank you goes for everyone in the office room of 6405 at LUT for coffee break pastimes and making every workday better than the one before. I also thank the door of 6405 for its apt comments upon arrival to the room. Special thanks for Associate Professor Mikko Kuisma on his valuable life lesson on assumptions that I have taken to heart.

Of course none of this would have been possible without the support of my family and friends. Thank you.

Janne Jäppinen
October 2019
Lappeenranta, Finland

Contents

Abstract

Preface

Contents

Nomenclature	8
1 Introduction	9
1.1 Research problem	9
1.2 Methods	10
2 Mixed-Flowing Gas (MFG) tests	12
2.1 Environmental classes and associated test conditions	12
2.1.1 Corrosion types	13
2.1.2 Group 2 conditions	14
2.1.3 Group 3 conditions	16
2.1.4 Other conditions	16
2.2 Corrosive Gases	17
2.2.1 Hydrogen sulfide (H ₂ S)	17
2.2.2 Sulfur dioxide SO ₂	17
2.2.3 Nitrogen dioxide (NO ₂)	17
2.2.4 Chlorine (Cl ₂)	18
3 Measurement principles and analyzers	19
3.1 UV-Fluorescence Spectroscopy	20

3.2	Conductometry	21
3.3	Colorimetry	21
3.3.1	Chemcassette	22
3.4	Flame Photometric	22
3.5	Gold film sensor	23
3.6	Chemiluminescence	23
3.7	Electrochemical	24
3.8	Ionic chromatography	24
3.9	Reflectometric	25
3.10	Cavity Attenuated Phase Shift	25
4	Results: Uncertainty Analysis of Selected Analyzers	26
4.1	Sulfur Dioxide (SO ₂)	26
4.2	Hydrogen Sulfide (H ₂ S)	28
4.3	Nitrogen dioxide (NO ₂)	30
4.4	Chlorine (Cl ₂)	32
5	Conclusion & Discussion	33
	References	35

Nomenclature

Abbreviations

Cl ₂	Chlorine
H ₂ S	Hydrogen sulfide
NO ₂	Nitrogen dioxide
SO ₂	Sulfur dioxide
ASTM	American Society for Testing and Materials
CAPS	Cavity Attenuated Phase Shift, a measurement method for NO ₂ .
CRDS	Cavity Ring Down Spectroscopy, a measurement method upon which Cavity Attenuated Phase Shift is based on.
EC	Electrochemical, a measurement principle.
EIA	Electronic Industries Alliance
FPD	Flame photometric detection, a measurement principle
IEC	International Electrotechnical Commission
MFG	Mixed Flowing Gas
pbb	Parts-per-billion
UV	Ultraviolet

1 Introduction

In this thesis suitable measurement methods for trace-level gases H₂S, SO₂, NO₂ and Cl₂ concentrations are presented and their merits are assessed. As background an introduction is given to the world of environmental mixed flowing gas (MFG) testing for the reliability of electronic components and systems. The measurement of parts-per-billion (ppb) trace-level gas concentrations is covered. Suitability of different measurement methods for MFG testing are assessed and suitable methods are chosen.

69% of electricity used in industry is by electric motor systems which power pumps, fans, compressors among many other applications (de Almeida, 2003). Electric motors are commonly used in process manufacturing where bulk materials have to be moved from one stage to another. Should any drive fail in the process the whole line has to be shut down which can be very costly ranging on a daily average of 100 000 € for a chemical production facility to 200 000 € for a paper or pulp plant (Baglee et al., 2017).

One reason for drive failure is caused by the environment in which it is running. Poor temperature and humidity control and pollution in industrial areas are a cause for corrosion to the equipment. It is not uncommon in process manufacturing sites to have a faint smell of chemicals like that evidenced around pulp mills. Some gases are witnessed by the smell but other gases may be present in such low quantities that they don't even cast an odour.

The concentration of gases around industrial sites was extensively obtained by William Abbott and his team and four classes of severity was proposed according to failure method of electrical contacts (Abbott, 1988) corresponding to severity of the site. Realistic, accelerated environmental testing method for industrial electronics was presented in the paper which correspond to earlier measurements around sites. These mixed flowing gas tests cause corrosion as found in these sites.

1.1 Research problem

The gas concentrations used in mixed flowing gas test are listed as trace-level parts-per-billion (ppb) units. The magnitude of ppb can be "visualised" with an analogy that a part per billion concentration is achieved with a drop of ink in one of the largest gasoline hauling tanker trucks (Satterfield, 2004). This means that specialized trace-level capable analyzers have to be used. Standards listed in chapter 2.1 list many kinds of measurement methods for each gas but their suitability is not addressed.

Presented here are the research questions of this thesis:

- What are the different gas concentration measuring methods for this application and

how do they compare?

- What are the main sources of uncertainty and how much uncertainty can be allowed to get meaningful results?
- How does the surrounding environment affect the measuring of gas concentrations?

1.2 Methods

Research methods include literature study on the overall view of mixed flowing gas tests and the associated gas concentration measurement methods. Gas analyzer performance is assessed by means of uncertainty comparison done according to the GUM: Guide to the Expression of Uncertainty in Measurement (JCGM, 2008).

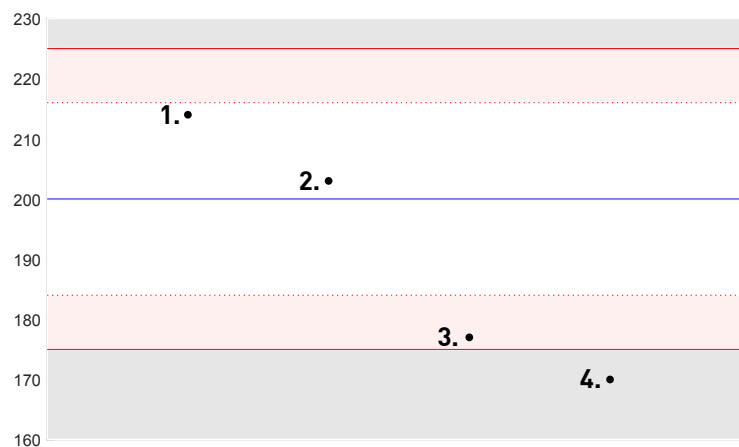


Figure 1.1: Graph of an arbitrary gas concentration of 200 ± 25 pbb with red shaded area of 9 pbb of uncertainty. Data points 1 & 2 in white area are acceptable, point 3 in the uncertainty margin and point 4 clearly over the gas concentration limit.

The gas concentrations are given as ranges that must be adhered to (e.g. 200 ± 25 pbb). A measurement value has a calculated uncertainty from specifications of the analyzer (e.g. 212 ± 9 at confidence level of 95 %). Thus to say that a measured value is between the gas concentration range the uncertainty subtracts the range at which the gas concentration can vary. This is illustrated in figure 1.1 where a red shaded area reduces the range where the measured value may vary to be considered to be in the concentration range.

An analyzer with better performance gives more room for gas supply variations including uncertainty of mass flow meter and gas cylinder concentrations given by the manufacturer. Uncertainty of gas supply system mass flow meters and gasses themselves are out of the scope of this work but very important to handle before the tests start.

Certain criteria have to be met by the analyzers to be included in the comparison. These include having a suitably low trace-level range, rack-mountability as opposed to a room-sized apparatus, not being overly expensive (< 10 000 €) and availability. Also non-suitable methods are out of the scope of this work.

2 Mixed-Flowing Gas (MFG) tests

In mixed-flowing gas testing electrical components are exposed to up to four pbb-level gases including hydrogen sulfide (H₂S), sulfur dioxide (SO₂), nitrogen dioxide (NO₂) and chlorine (Cl₂) to simulate effects in industrial areas and to accelerate corrosion. As first presented in (Abbott, 1988) the tests were soon published as guidelines and standards by IEC 60068-2-60 (2015), ASTM B845-97 (2013), EIA 364-65B (2009) and Telcordia GR-63-CORE (2012).

2.1 Environmental classes and associated test conditions

According to Abbott (1988) the pre-existing environmental tests were too unrealistic and severe that they produced unrealistic results or did not represent indoor field conditions at all. These older tests included testing with a single gas with a high concentration and using too high a temperature and humidity. The main finding was that concentration data gathered outdoors was too high compared to the exposure of electronics inside buildings and in enclosures. The concentrations in real indoor installations was found to be in the order of 10-100 parts-per-billion (pbb) per pollutant.

Four classes of different field environments was recognized by Abbott (1988) based on data gathered around the world from industrial sites. These were dubbed Battelle Classes I-IV in order of severity with class I having no effect on electronics and class IV representing the most severe of conditions. Test conditions are presented in table 2.1 ordered by severity and grouped by similarity. From the table it can clearly be seen that the work conducted by Abbott was a foundation on which different standard issuers based their MFG tests albeit with a few modifications. As no corrosion appears in Class I conditions there's no test for it and it is omitted from the table.

The environmental classes are derived from reactivity monitoring copper coupons exposed to thousands of different industrial locations around the world (Abbott, 1988). The amount of corrosion was measured as weight gain and thickness of corrosion layer in the coupons. The chemical composition of corrosion layer and the corrosion mechanism were studied and then recreated in a laboratory setting. When the same amount of corrosion was achieved the test conditions were varied precisely to achieve a plausible acceleration. Similar coupon tests have also been conducted with gold plated copper coupons with a layer of nickel between, as thin films of gold are commonly used in electric contacts (Abbott, 1987).

Many standards and guidelines, seemingly based on Abbotts work include:

- ASTM B827-05 (2014), Standard Practise for Conducting Mixed Flowing Gas (MFG) Environmental Tests (ASTM B827-05, 2014)

- ASTM B845-97 (2013), Standard Guide for Mixed Flowing Gas (MFG) Tests for Electrical Contacts (ASTM B845-97, 2013)
- IEC 60068-2-60:2015, Environmental testing - Part 2-60: Tests - Test Ke: Flowing mixed gas corrosion test (IEC 60068-2-60, 2015)
- EIA 364-65 (2009), TP-65B Mixed Flowing Gas Test Procedure for Electrical Connectors Contacts and Sockets (EIA 364-65B, 2009)
- Telcordia GR-63-CORE Issue 4 (2012), NEBS™ Requirements: Physical Protection (Telcordia GR-63-CORE, 2012)

Test conditions from each standard are given in table 2.1 where they are grouped by similarity by the author of this thesis. These conditions mostly follow the Battelle severity classes established in (Abbott, 1988) and the grouping is based on the apparent similarity of test conditions i.e. matching gas concentrations, temperature and relative humidity. Listed below are the few exceptions between the Battelle classes and the rest of the standards:

- (ASTM B827-05, 2014) and (ASTM B845-97, 2013) lists all the rest of the standards and gives guidance on how to use each.
- (IEC 60068-2-60, 2015) contains Battelle class II test with slightly modified humidity and tolerances (Method 2) and with added SO₂ (Method 4).
- (EIA 364-65B, 2009) contains the Battelle classes II and III superseded with their Class IIA and IIIA specifications with slightly differing tolerances and added SO₂ as compared to Battelle.
- (Telcordia GR-63-CORE, 2012) contains Battelle class II conditions in Indoor specification and Battelle class III conditions in Outdoor specification with both having added SO₂.

A thing to note is that though higher classes are more severe, class III conditions do not also represent Class II conditions (Abbott, 1988). The different classes have different corrosion mechanisms and products. So for "full coverage" one must test with all the test classes or just use the one related to the applications severity level.

2.1.1 Corrosion types

The main corrosion types are pore and creep corrosion. Contact surfaces plated with a thin precious metal film are prone to pore corrosion (see figure 2.1) driven by chlorides. As the plating is thin it can easily contain pores which expose the layer under to the

environment causing corrosion. The base metal may diffuse through the pores and allow a reaction with oxygen and chemicals present in the air. Then the corrosion products begin to migrate out of the pores over the precious metal plating (Liu and Pecht, 2004).

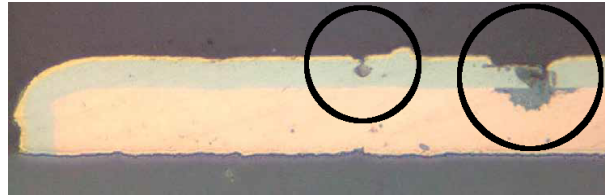


Figure 2.1: Cross-section of pore corrosion through the gold plating (left) and through gold plating and nickel layer (right) in an electrical connector. (Vogel et al., 2015)

Creep corrosion (see figure 2.2) has an effect similar to pore corrosion where scratches and edges in the noble coating expose the base metal to corrosive gases and oxygen. Creep corrosion is driven mostly by sulfides but chlorine accelerates the process. The corrosion then spreads over the plating or over dielectric surfaces at worst causing short-circuits. It also contributes to increased resistance across contacts surfaces (Liu and Pecht, 2004).

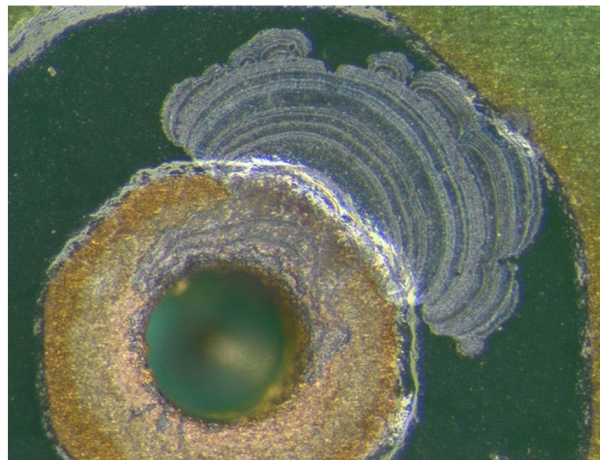


Figure 2.2: Creep corrosion around an through-hole in a printed circuit board. (Vogel, 2016)

2.1.2 Group 2 conditions

Group 2 test conditions represent a mild corrosive area such as business offices and control rooms in light industrial areas (ASTM B845-97, 2013). The main corrosive effect is pore corrosion on gold platings and corrosive films with $\text{Cu}_x\text{O}_2\text{Cl}_z$, Cu_2O and Cu_2S over copper coupons (Abbott, 1988). The exact chemical composition of these chloride copper compounds is not known. This reactive chloride was found in 45 to 55 % of field sites in Abbott's work but IEC 60068-2-60 (2015) claims that Cl_2 is rarely observed in the

Table 2.1: Mixed Flowing Gas test conditions from each standard grouped by the similarity of conditions.

Standard	T [°C]	RH [%]	H ₂ S [ppb]	Cl ₂ [ppb]	NO ₂ [ppb]	SO ₂ [ppb]
Group 2						
Battelle Class II	30 ± 2	70 ± 2	10 + 0/-4	10 + 0/-2	200 ± 25	
EIA-364-65 Class IIA	30 ± 1	70 ± 2	10 ± 5	10 ± 3	200 ± 25	100 ± 20
IEC60068-2-60	30 ± 1	75 ± 3	10 ± 5	10 ± 5	200 ± 50	
Method 2						
IEC60068-2-60	25 ± 1	75 ± 3	10 ± 5	10 ± 5	200 ± 20	200 ± 20
Method 4						
Telcordia GR-63-Core Section 5.5 Indoor	30 ± 1	70 ± 2	10 ± 1.5	10 ± 1.5	200 ± 30	100 ± 15
Group 3						
Battelle Class III	30 ± 2	75 ± 2	100 ± 10	20 ± 5	200 ± 25	
EIA-364-65 Class IIIA	30 ± 1	70 ± 2	100 ± 10	20 ± 5	200 ± 25	200 ± 50
IEC60068-2-60	30 ± 1	75 ± 3	100 ± 20	20 ± 5	200 ± 50	
Method 3						
Telcordia GR-63-Core Section 5.5 Outdoor	30 ± 1	70 ± 2	100 ± 15	20 ± 3	200 ± 30	200 ± 30
Others Group						
Battelle Class IV	50 ± 2	75 ± 2	200 ± 10	50 ± 5	200 ± 25	
IEC60068-2-60	25 ± 1	75 ± 3	100 ± 20			500 ± 100
Method 1						

field and even Abbott (1988) doubts its significant presence but recognizes that a form of reactive chloride is present. For more information see chapter 2.2.4.

All the standards included in table 2.1 list the concentration of hydrogen sulfide (H₂S) at 10 ppb, chlorine (Cl₂) at 10 ppb, nitrogen dioxide at 200 ppb and, if included, sulfur dioxide at 100 or 200 ppb. Temperatures used vary between 30°C and 25°C with relative humidities at 70 or 75 %.

Abbott (1988) goes to great lengths to stress the importance of low enough H₂S concentration to not change to Battelle Class III corrosion mechanisms and recommends the control of the concentration at or below 10 ppb. Interestingly standards other than Battelle have less tight ranges for each gas. It is noted in (Abbott, 1988) that it is critical for Cl₂ concentration to be kept at or below 10 ppb to not get unrealistic results. Why the rest of the standards (see table 2.1) allow ±3 to ±5 variance is not explained in the standards.

The NO₂ concentration level is said to not be critical and that a level at or above H₂S concentration is sufficient. Also the original Battelle classes contain no SO₂ as it is believed not to have any effect on the tests. Still it is stated in (Abbott, 1988) that SO₂ may be included to account for new materials not included in the original tests. It would seem so that EIA, IEC and Telcordia have added the SO₂ for that reason as seen in table 2.1.

2.1.3 Group 3 conditions

Group 3 test conditions correspond to moderate amounts of pollution found in industrial sites and in the close vicinity of industrial sites e.g. storage areas nearby (ASTM B845-97, 2013). In these areas primary pollution sources are nearby and affect all the businesses in the region and coupled with poorly controlled environments cause pore corrosion and creep corrosion films on metal surfaces. Corrosion product on copper coupons corrosion films is mainly Cu₂O and Cu₂S with Cu_xO₂Cl_z.

Table 2.1 list the Group 3 conditions as concentrations of hydrogen sulfide (H₂S) at 100 pbb, chlorine (Cl₂) at 20 pbb, nitrogen dioxide (NO₂) at 200 pbb and, if included, sulfur dioxide (SO₂) at 200 pbb. Temperature used in all is 30°C and relative humidities vary between 70 and 75 %.

At Group 3 conditions the control of H₂S concentration level is less critical as the mechanism has changed from Group 2 and only limited acceleration is available with added H₂S. Chlorine level in group 3 conditions is also not so critical but a maximum of 25-30 pbb shall not be exceeded. NO₂ concentration remains the same as in group 2 and the control is not critically exact. For SO₂ the same applies as in group 2, where SO₂ may be added to take into account new materials. (Abbott, 1988)

2.1.4 Other conditions

Battelle class IV conditions correspond to severe amounts of pollution at or very near a pollution source with a high humidity. Testing for this environment is said to be not recommended as material selection of contact surfaces or other remedies are rarely sufficient to protect the surfaces (ASTM B845-97, 2013). The main corrosion product on noble metals is creep corrosion and corrosion film on copper coupons consists mostly of Cu₂S (Abbott, 1988).

IEC60068-2-60 method 1 is for testing gold-plated surface contacts in mild environments (IEC 60068-2-60, 2015). As no other test has these conditions this method seems like an outlier and thus is in the others group. No additional information on effects or mechanisms can be found than those said in the standard. Interestingly Abbott (1988) has emphasized the use of Cl₂ and NO₂ to produce realistic results and recommended against the use of arbitrarily high SO₂ and H₂S concentrations.

2.2 Corrosive Gases

2.2.1 Hydrogen sulfide (H₂S)

Hydrogen sulfide H₂S is a colorless, heavier than air toxic gas that has the smell of rotten eggs (Pouliquen et al., 2000). Aside from natural sources it is formed as a degradation product in paper industry during pulp production, agricultural food industry and in slaughterhouses. H₂S is used to produce elemental sulfur from natural gas, in the production of metal sulfides and in analytical chemistry to name a few.

Hydrogen sulfide has a corrosive effect on silver and copper (IEC 60068-2-60, 2015) and Abbott (1988) considers it to be the main driver in sulfide reactions of Battelle classes III (Group 3) and IV (Others). Also noted in (Abbott, 1988) is that H₂S concentration in Group 2 conditions have to be kept below 15-20 ppb to not change to Group 3 mechanisms.

2.2.2 Sulfur dioxide SO₂

Sulfur dioxide SO₂ is a toxic colorless gas with a pungent odor and an acid taste. Sulfur dioxide is the first step in the production of sulfuric acid and the majority of sulfur dioxide is used for this purpose. Aside from producing sulfuric acid SO₂ is also used for various chemical purposes in paper and pulp industry, chemical and pharmaceutical, petrochemical and mineral oil, textile and leather, and food and beverage industries. Large amounts of SO₂ is released in the air by combustion of sulfurous fossil fuels. (Müller, 2000)

In (Abbott, 1988) it is shown that SO₂ produces no measurable effects on corrosion and is used in environmental tests on a historical basis as it was the foundation of previous single gas environmental tests. Indoor levels of SO₂ were found to be on the level of that of H₂S and that high outdoor levels are greatly attenuated in indoors or in sheltered (case of a electronic device) conditions. Because of having no effect SO₂ is not included in any of the original Battelle tests but as seen in table 2.1 it is included in most others. In IEC 60068-2-60 (2015) regarding Method 1 a synergistic effect between SO₂ and H₂S is claimed, but the basis of this is unclear.

2.2.3 Nitrogen dioxide (NO₂)

Nitrogen dioxide is a highly toxic brownish red gas with irritating pungent odor. NO₂ is a major air pollutant as it is produced in all combustion processes and is a major component in photochemical smog (Thiemann et al., 2000).

In mixed-flowing gas tests NO₂ plays no direct part in corrosion but is an accelerant to

sulfur reactions on silver and copper (Abbott, 1988). Abbott (1988) theorizes that NO_2 could be an oxidizing agent for H_2S and in IEC 60068-2-60 (2015) it is said that NO_2 is used as an oxidant. NO_2 seems to accelerate creeping corrosion but only small amounts like 50 pbb is enough and large variations do not produce more acceleration. As seen in table 2.1 NO_2 concentration is 200 pbb in all the test types.

2.2.4 Chlorine (Cl_2)

Chlorine is a pungent, greenish-yellow, toxic gas which is highly reactive with most elements and is rarely found in the free state (Schmittinger et al., 2011). Cl_2 is used in bleaching agents, water sterilizing and in numerous chemical intermediates and end products including polyvinyl chloride (PVC) plastic. It is also used in many solvents and pesticides with 96% of crop protection chemicals and 90% of pharmaceuticals in Europe (2005) are produced using chlorine.

Abbott (1988) states that Cl_2 should be regarded as a convenient laboratory chemical to drive corrosion and produce similar chemistries as in the field. It is also speculated that using Cl_2 may simulate reactions caused by other halogenated compounds found in different sites but these speculations are without clear evidence. The role of Cl_2 is not precisely understood but analytical evidence suggests that Cl_2 attacks the natural Cu_2O film on copper and may be to regulate the pH of the surface film. Precise control of Cl_2 concentration is stressed as to not produce unrealistic reactions.

3 Measurement principles and analyzers

Gas concentrations can be measured with numerous different measurement principles. In this chapter the measurement principles applicable to mixed flowing gas tests are presented and suitable methods are chosen. Table 3.1 lists the different methods as given by IEC 60068-2-60 (2015) and ASTM B827-05 (2014). Also listed in the table are a few methods outside these standards that could be suitable for low concentration gas analysis.

Table 3.1: Suitable measuring methods for each gas.

Method / Chemical	SO ₂	H ₂ S	NO ₂	CL ₂
UV-fluorescence	xy	xy		
Conductometry	x	x		
Colorimetry	x	x	x	x
Chemcassette	z	z	z	z
Flame Photometric	y	xy		
Adsorption on gold film		x		
Chemiluminescence			xy	
Electrochemical				xy
Ionic chromatography				x
Reflectometric				y
Cavity Attenuated Phase Shift			z	

x = IEC 60068-2-60 (2015)
y = ASTM B827-05 (2014)
z = Methods found through own research

Suitable measuring methods for sulfur dioxide (SO₂) and hydrogen sulfide (H₂S) are listed in (ASTM B827-05, 2014) as photometric meaning flame photometric, and luminescence used as an umbrella term for fluorescence. (IEC 60068-2-60, 2015) further lists UV-fluorescence, conductometry and colorimetry for SO₂ and additionally adsorption on gold film for H₂S as seen on table 3.1. When searching suitable analyzers it seemed that UV-fluorescence is de facto for these kinds of low concentrations - even so that the European Standard for monitoring SO₂ in ambient air (EN14211) uses UV-fluorescence as the measuring method. H₂S is not commonly measured in ambient air but (Kourtidis et al., 2008) used an UV-fluorescence based analyzer in their ambient measurements.

For nitrogen dioxide both (IEC 60068-2-60, 2015; ASTM B845-97, 2013) list chemiluminescence and ASTM additionally lists colorimetry. During the search for NO₂ analyzers a more recent kind of method also appeared - Cavity Attenuated Phase Shift Spectroscopy or CAPS for short. CAPS-type analyzer manufacturer Teledyne (Teledyne, 2016) promises fast response and high sensitivity but uncertainty calculations and com-

parison in chapter 4.3 proves that this method is not as good as the well established UV-fluorescence type of measurement.

For chlorine (ASTM B827-05, 2014) lists colorimetry, electrochemical and ionic chromatography as suitable methods. The Chemcassette system is based in colorimetry but is included as a separate entity as the other colorimetric methods rely on absorbing the analyte to a solution and to clarify that the Chemcassette system is assessed only for Cl_2 . (IEC 60068-2-60, 2015) too lists electrochemical and also reflectometric method for chlorine detection.

The following subchapters briefly introduces the available measurement methods. Reasons to include the method and the associated analyzer in further uncertainty assesment are given in each subchapter. Chapter 4 contains the uncertainty analysis for the analyzers deemed most suitable.

3.1 UV-Fluorescence Spectroscopy

Fluorescence is a phenomenon where visible or ultraviolet light excites a fluorescent material which then emits the absorbed energy as light. Different substances absorb energy at different wavelengths and usually emit the energy at a longer wavelength. In fluorescent spectroscopy a controlled light source is used to excite the analyte and a photomultiplier is used to record the emission spectrum. As different substances absorb and emit at different wavelengths this allows to tune the instrument to a specific substance as long as it is fluorescent material. (Lakowicz, 2006; Nielsen, 2017)

As can be seen in table 3.1 both SO_2 and H_2S can be measured with this method. Analyzers for SO_2 include the Thermo Scientific 43i and Ecotech Serinus 50 whose uncertainties are analyzed in chapter 4.1. Measurement of H_2S concentration in air is done by first scrubbing out SO_2 in the air and then thermally converting H_2S to SO_2 which is then analyzed by UV-fluorescence spectroscopy as SO_2 . This SO_2 then directly correlates to H_2S concentration. Ecotech offers both an H_2S -only analyzer Serinus 55 and a combination device Serinus 51 which is able to measure both SO_2 and H_2S back-to-back. Thermo Scientific also offers a similar combination device 450i.

It is shown in (Bluhme et al., 2016) that humidity affects the measurement of H_2S where more than 34 % of test gas concentration of H_2S was undetected at a relative humidity of 80 %. Also measured was the effect of humidity on the measurement of SO_2 but no interference was found. As the humidity doesn't affect the SO_2 measurement it is possible that the thermal converter used is affected by the humidity. Though the test concentration of 573 ± 3 pbb is high compared to concentrations seen in table 2.1 of 10, 100 and 200 pbb this effect still has to be analyzed for MFG application.

An 10 % decrease in fluorescence intensity was found in (Matsumi et al., 2005) where

a concentration 10 pbp of SO₂ was measured. This difference between (Matsumi et al., 2005) and (Bluhme et al., 2016) could be attributed to differences in equipment. It still means that the effect would still have to be tested for application in MFG tests.

3.2 Conductometry

Using conductometric measurement the analyte is dissolved to a solution of a known conductivity where the analyte changes the conductivity of said solution. The temperature and total ions in solution affects the measurement thus it could be affected by the other gasses in the chamber. By looking at research on conductometry it seems quite outdated as most cited scientific papers regarding the subject are from the 60's to 80's like (Asmus et al., 1970), (Urone et al., 1965), (Symanski and Bruckenstein, 1986), (Zipp and Evers, 1969) and during initial search for SO₂ and H₂S analyzers none came up with conductometric detection. No further consideration for conductometry as a measurement method is given in this thesis.

3.3 Colorimetry

Using a colorimeter for SO₂ analysis it is absorbed to a solution of sodium tetrachloromercurate, and additional formaldehyde and a pararosaline dye to form a strong purple dye complex. A light source is used to illuminate the sensing and reference cells where photocells sense the color of the analyte which is compared to the colour of the reference thus giving a concentration value. (Liptak, 2003)

The problem with SO₂ colorimetry is the maintenance of its complex plumbing and and the sensing cell. The sensing cell loses sensitivity as the dye complex plates out to sensing cell windows. A colorimeter is highly selective as it is based on a chemical reaction between SO₂ and sodium tetrachromercurate. (Liptak, 2003)

H₂S colorimetry involves the reaction of H₂S to a chemically selective tape which is then compared to a blank tape to give a concentration reading (Sick Maihak GmbH, 2012). Mostly these devices are for petroleum industry as evidenced by the product sheet of Analytical Systems Keco Series 150-lab (Keco, 2015). In the sheet the standards complied are listed as ASTM D4082-82, D4468-85 and D4045-81, which all are standards relating to H₂S measurement in the petroleum industry. Sicks Monocolor 1N and 2Ex product sheet does list ambient air in typical applications but mostly applications relate to heavy industry and gas production (Sick Maihak GmbH, 2012).

According to (Liptak, 2003) colorimetric analysis of nitrogen dioxide (NO₂) can be done with the Griess-Saltzman (GS) or the Jacobs-Hochheiser (JH) method. In both methods the air containing NO₂ is passed into a solution which changes color based on the amount

of NO₂ passed. Compared to most other methods these are very slow with continuous GS analyzer having a 5 to 15 minutes response time and JH is used with longer duration integrated samples up to 24 hours (Liptak, 2003). No analyzers of this type was found in the internet and the procedure seems more suitable for chemistry labs studying air pollution.

With these complexities and being out of MFG application these colorimetric methods are given no further consideration.

3.3.1 Chemcassette

Colorimetric determination of chlorine can also be done with Honeywell SPM Flex Chemcassette system where a paper tape is impregnated with substance that changes color when exposed to chlorine (Honeywell, 2016). After a concentration is measured the tape is advanced to a fresh patch of tape to allow the next measurement. The Chemcassette system would allow the measurement of SO₂, H₂S and NO₂ by changing the tape cartridge but as the uncertainty analysis in chapter 4.4 shows the performance is quite poor and other methods are more suitable for these gases.

3.4 Flame Photometric

In flame photometric detection (FPD) the gas to be analyzed is excited to a higher energy level by a hydrogen and oxygen rich flame after which it returns to ground state producing a gas specific emission spectrum which is then recorded by a photomultiplier tube and analyzed to give a concentration value (Liptak, 2003). Chromatotec provides a FPD which is certified for determination of sulfur compounds in natural gas (ISO 19739:2004) (Chromatotec, 2006) and ABB provides similar total sulfur analyzer PGC5007 (ABB, 2017) which is covered by a similar standard (ASTM D7041 - 04) for light hydrocarbons, motor fuels and oils.

Though Chromatotec claims ambient air analysis as a market for their product no performance characteristics are given regarding e.g. accuracy. ABB does not mention ambient air measurement at all and lists some of its characteristics regarding analyzing of total sulfur from diesel oil. Knowing the amount of total sulfur is not useful in MFG tests since we are going to use two sulfur compounds. No prices are given but (Liptak, 2003) gives an estimate ranging from \$35,000 to \$45,000 which is out of the price range given in chapter 1.2. As such the FPD method is given no further consideration.

3.5 Gold film sensor

With a gold film sensor hydrogen sulfide adsorbs into gold which causes the gold films resistance to increase proportionally to the mass of absorbed H_2S (Liptak, 2003; Arizona Instrument LLC, 2017). Only one manufacturer of this kind of analyzer was found, AMETEK Arizona Instrument LLC, with a portable model and a stationary one for use in outdoors. These are not meant for MFG tests but rather for personal and industrial plant safety. Without high enough specifications this kind of measurement principle is deemed unusable.

3.6 Chemiluminescence

Chemiluminescence is a phenomenon where as a result of a chemical reaction photons are released (Bergamini et al., 2016). As there is no need for an external excitation like in the case of fluorescence (chapt. 3.1) nor filters to select correct wavelengths, there's virtually no background noise in the measurement except for the noise of the photomultiplier tube used to record the amount of photons. The noise can be very low in the case of optimized detectors for low light levels which results in a high signal-to-noise ratio.

In the case of NO_2 measurement the NO_2 is first converted to NO using a catalytic converter. When the resulting NO is reacted with an excessive amount of O_3 the NO reacts form NO_2 in an electronically excited state. As the excited NO_2 returns to ground state photons are released. The amount of light released is directly proportional to NO in sample thus an NO_2 concentration can easily be determined (Liptak, 2003).

In (Visamo, 2009) the effect of water vapour on a Environnement AC31M-LCD analyzer which uses chemiluminescence as the measuring principle was found. It was found that with a relative humidity of 90 % the NO_2 reading was 465 pbb and with dry NO_2 sample the reading was 524 thus creating a deviation of -59 pbb. This was found non-compliant with SFS-EN14211 though the standard calls for a relative humidity of 80 %. It was also concluded that the sample humidity was the largest contributor to the en14211 defined uncertainty. (Visamo, 2009)

Effect of water vapour is also documented in (Marta Doval Miñarro, 2012) where NO_2 analyzers from time before the standard EN14211 were studied to see if they pass the requirements set in the standard. In the article it is said that the effect of water vapour comes from overlapping emission spectrum for excited NO_2 (600-3000 nm) and absorption spectrum for water vapour (from 750 nm on). Water vapour interference was identified as most important contributor to expanded uncertainty along with long term drift and sample pressure. Effect of water vapour could possibly be reduced by using a humid calibration gas. (Marta Doval Miñarro, 2012)

This method is included in the uncertainty analysis presented in chapter 4.3 and is the

only method for NO₂ analysis mentioned in ASTM B827-05 (2014). The analyzer to be assessed is Ecotech Serinus 40 which is an oxides of nitrogen (NO, NO₂) analyzer with a range of 0-20 ppm. The analyzer is certified according to EN 14211:2012 for ambient air measurement of nitrogen dioxide and nitrogen monoxide by TÜV Rheinland (Ecotech, 2018).

3.7 Electrochemical

An electrochemical (EC) sensor works by producing a current in proportion to the gas concentration via an appropriate chemical reaction. Electrochemical sensors are mostly used in handheld personal toxic gas alarms given their somewhat small size and inexpensive price (Wrenn, 2014). Electrochemical sensor is listed in (IEC 60068-2-60, 2015) and (ASTM B827-05, 2014) as a method for Cl₂ concentration analysis.

There are many problems with using electrochemical sensors in MFG tests trace-level application. One is that most sensors are discrete components needing the measurement electronics to work and that the sensor needs to be inside the MFG chamber. No analyzers with external tubing could be found. Second problem is that of too high a minimum detection limit as seen in the datasheet (Nemoto Sensor Engineering Company Ltd, 2016) being 0,1 ppm. Third problem is that electrochemical sensors mostly achieve a resolution of only 1 ... 0,1 ppm (Wrenn, 2014). Both of these numbers are too low for detecting the Cl₂ concentrations as seen in table 2.1 ranging from 10 pbb to up to 50 pbb.

Also noteworthy is cross-sensitivity of the sensor which is dependent on the chemistry of the sensor. For Nemoto NE4-CL2 the datasheet states a 100 % cross-sensitivity to NO₂ and below -400 % and -100 % cross-sensitivity to H₂S and SO₂ respectively (Nemoto Sensor Engineering Company Ltd, 2016). As NO₂ and H₂S are present in all the tests this would be highly problematic. But different chemistries for EC sensors exist. If using a Dräger DrägerSensor® XXS Cl₂ the cross-sensitivities are less of a problem but they still exist for the gases for the MFG tests.

With these inherent minimum detectability, resolution and cross-sensitivity problems the electrochemical measurement principle cannot be applied in chlorine sensing in MFG test application.

3.8 Ionic chromatography

In ionic chromatography for chlorine (Cl₂) the gas to be analyzed is dissolved to a suitable liquid to produce chloride ions Cl⁻ which is then run through a column (Askew, 1989). In general ion chromatography different components of the sample pass through the column at different speeds. After a known time a suitable detector can detect the concentration of

ions (Liptak, 2003) and therefore the amounts of components in the sample.

For MFG application this would be too arduous as a measuring method - as the Cl concentration in the test chamber is very low a large sample of chlorine is needed to pass through the capturing liquid to produce meaningful results (Askew, 1989). The device itself is quite costly ranging from \$35,000 to \$45,000 according to (Liptak, 2003) and up to 20 minutes of time per sample is needed.

3.9 Reflectometric

The ASTM B827-05 (2014) mentions reflectometry as a suitable chlorine concentration test method and cites an ASTM test method as a suitable procedure. The cited method is D2912 "Test Method for Oxidant Content of the Atmosphere" which was withdrawn in the year 1990 with no replacement (ASTM, 1976). The test method is also not specific to chlorine but for other oxidants as well.

As the measurement principle in ASTM D2912 remains unclear because the document is not available, the only result search for chlorine reflectometry is for determination of chlorine in liquids. As mentioned in (Millipore, 2015) the reflectometer is for food and beverage chemicals monitoring and has nothing to do with gas analysis. A reflectometer from Dräger Corporation is cited in (Ralfs, 1997), but the original citation is unavailable and it is noted that accurate determination of chlorine below 200 pbb is not possible rendering it unusable in MFG application.

3.10 Cavity Attenuated Phase Shift

Cavity Attenuated Phase Shift (CAPS) spectroscopy is a variant of Cavity Ring Down Spectroscopy (CRDS) (Kebabian et al., 2007). In CRDS a light source is used to produce light between two highly reflective mirrors until a detector senses a high enough level. Then the light source is shut down and the light is allowed to ring down via scattering, reflection from the mirrors and attenuation caused by the analyte gas (Liptak, 2003).

Whereas CRDS is time-based the CAPS method differs from this approach as that a phase shift between square-wave modulated led and distorted waveform from the detector is measured which gives the concentration reading. The CAPS method is said to not be interfered by humidity in the sample as is the case in chemiluminescence (see chapt. 3.6).

Teledyne T500U is an analyzer utilizing the CAPS method. The CAPS method directly measures the concentration of NO₂ (Teledyne, 2016) as opposed to chemiluminescence where NO₂ is first converted to NO and then the concentration is measured. Uncertainty of Teledyne T500U is assessed in chapter 4.3 where it is compared to chemiluminescence.

4 Results: Uncertainty Analysis of Selected Analyzers

Uncertainties are assessed for most suitable analyzers based on the review of measuring methods in the previous chapters. The analyzers are listed in table 4.1. Main sources of uncertainty are identified and overall suitability of the analyzer is assessed. Type B uncertainty is evaluated from the available data according to the Guide to the Expression of Uncertainty in Measurement. This data consists of user manuals and technical datasheets provided by the manufacturers.

Table 4.1: The analyzers chosen in chapter 3 for uncertainty analysis.

Gas	Measurement principle	Analyzer
SO ₂	UV-fluorescence spectroscopy	Ecotech Serinus 50
	UV-fluorescence spectroscopy	Thermo Scientific 43i
H ₂ S	UV-fluorescence spectroscopy	Ecotech Serinus 55
	UV-fluorescence spectroscopy	Thermo Scientific 450i
NO ₂	Cavity Attenuated Phase Shift	Teledyne T500U
	Chemiluminescence	Ecotech Serinus 40
Cl ₂	Chemcassette (colorimetry)	Honeywell SPM Flex

As explained in the chapter 1.2 a higher uncertainty of an analyzer gives less room for the gas concentration to vary. Thus for analyzers using the same measurement principle the one with better performance should be chosen. Uncertainty analysis allows for comparison of methods as done with NO₂.

In the following subchapters the uncertainties are estimated by using the upper limit of the gas concentration range as the reading needed for calculations. This is termed simulated reading by the author for the sake of convenience. As stressed in (Abbott, 1988) that verification of test chamber gas concentrations is very important a confidence level of 99 % is used as basis in calculations.

4.1 Sulfur Dioxide (SO₂)

Uncertainty analysis for Sulfur dioxide analyzers Ecotech Serinus 50 and Thermo Scientific 43i both using UV-fluorescence spectroscopy (chapt. 3.1) is presented in table 4.2. SO₂ concentrations given in table 2.1 are 100, 200 and 500 pbb for the different test types. Uncertainties are calculated at the maximum concentration given by ranges in table 2.1 as to not estimate too low an uncertainty.

Table 4.2: Uncertainty analysis and comparison of Ecotech Serinus 50 and Thermo Scientific 43i UV-fluorescence type SO₂ analyzers. All uncertainty constituents are uniformly distributed.

		Ecotech Serinus 50		Thermo Scientific 43i			
		Specification	u_c	u_c	Specification	u_c	u_c
Simulated reading			600	220		600	200
Range		0 - 20 ppm (auto ranging)			0 - 1 ppm (selectable)		
Precision		0.5 ppb or 0.15 % of rdg.	0.52	0.29	1 % of rdg. or 1 ppb	3.46	1.27
Linearity		±1 % of full scale [†]	5.77	5.77	± 1% of full scale [†]	5.77	5.77
Noise at Zero		< 0.15 ppb	0.09	0.09	1.0 ppb RMS (10 s avg t.), 0.5 ppb RMS (60 s avg t.), 0.25 ppb RMS (300 s avg t.) [‡]	0.29	0.29
Zero drift (T dependant)		0.1 ppb per °C					
Zero drift (24 h)		< 0.5 ppb	0.29	0.29	< 1 ppb	0.58	0.58
Zero drift (30 days)		< 0.5 ppb	0.29	0.29			
Span drift (T dependant)		0.1 % per °C					
Span drift (24 h)		< 1 % of reading	3.46	1.27			
Span drift (30 days)		< 1 % of reading	3.46	1.27	± 0.5 %	1.73	0.64
Combined			6.76	5.93		6.98	5.98
Extended (k = 2.6)			17.57	15.41		18.15	15.55

[†] Full scale means the selected range and not the devices full scale according to both manufacturers. Here the uncertainty caused by linearity is calculated at a range up to 1000 ppb.

[‡]Noise at Zero for Thermo Scientific 43i calculated with a 60 s averaging time.

As can be seen in table 4.2 the performance characteristics given by Ecotech and Thermo Scientific vary only a little and combined uncertainties are about the same. For both the main source of uncertainty is linearity which is $\pm 1\%$ of full scale. According to both manufacturers the linearity is actually dependent on the range selected for which the analyzers are calibrated to.

Aside from the linearity error most of these sources of uncertainty cannot be eliminated as they are given only as singular values not depending on anything. This is to say that they remain the same regardless of reading or chosen range. The temperature dependant zero and span drift for Ecotech Serinus 50 can be mitigated by close regulation of air temperature surrounding the equipment. Noise at zero for Thermo Scientific 43i can be mitigated by choosing a longer averaging time but too long a time might not be usable depending on the measuring interval used in MFG testing.

For both analyzers measuring a concentration of 200 pbb results in an extended uncertainty ($k = 2.6$) of ± 16 pbb at confidence level of 99 %. As the concentration tolerances in table 2.1 vary from 15 to 50 the test with the tightest tolerance (Telcordia GR-63-Core Section 5.5 Indoor) cannot be done and tests with ± 20 tolerance don't have much headroom for gas concentration variation. As the original Battelle tests don't even have SO₂ as Abbott (1988) questions it's importance it could be argued that the headroom isn't really a problem. But it is also said that SO₂ can be included to take into account new materials used in electronics.

Uncertainty caused by linearity could be dropped significantly if the analyzers were to be calibrated at a lower range than 1000 pbb. 1000 pbb value for calculations was chosen due to IEC60068-2-60 Method 1 having SO₂ concentration up to 600 pbb but as the other tests use values 100 or 200 pbb with differing ranges the devices could be calibrated to a lower range e.g. up to 500 pbb. This would drop the extended uncertainties for both the devices down to 9 pbb making the test with the lowest concentration range viable from the measurements point of view.

Unsurprisingly these analyzers utilizing the same measurement principle have about the same uncertainty performance. As such either one of these analyzers could be chosen for MFG testing. In the end it would boil down to price and ease of maintenance.

4.2 Hydrogen Sulfide (H₂S)

Uncertainty analysis for Hydrogen sulfide analyzers Ecotech Serinus 55 and Thermo Scientific 450i both using UV-fluorescence spectroscopy (chapt. 3.1) like the SO₂ analyzers is presented in table 4.3. Test condition H₂S concentrations given in table 2.1 are 10, 100 and 200 pbb. Uncertainties are calculated at maximum concentration given by ranges in table 2.1 which is 210 pbb as per requirements of Battelle Class IV test as to not estimate too low an uncertainty.

Table 4.3: Uncertainty analysis and comparison of Ecotech Serinus 55 and Thermo Scientific 450i H₂S analyzers. All uncertainty constituents are uniformly distributed.

	Ecotech Serinus 55 Specification	u_c	Thermo Scientific 450i Specification	u_c
Range	0 - 20 ppm (auto ranging)		0 - 10 ppm (selectable)	
Precision	0.5 ppb	0.29		
Linearity	± % 1 of full-scale [†]	2.89	± 1 % of full-scale [†]	2.89
Noise at Zero			3.0 ppb RMS (10 s avg t.), 1.5 ppb RMS (60 s avg t.), 0.75 ppb RMS (300 s avg t.) [‡]	0.87
Zero drift (temperature dependant)	0.1 ppb per °C			
Zero drift (24 h)	< 1 ppb	0.58	< 1 ppb	0.58
Zero drift (30 days)	< 1 ppb	0.58		
Span drift (temperature dependant)	0.1 % per °C			
Span drift (24 h)	< 0.5 % of rdg	0.58	± 1 % full-scale	2.89
Span drift (30 days)	< 0.5 % of rdg	0.58		
Combined		3.01		4.21
Extended (k = 2.6)		7.84		10.95

[†] Like with the SO₂ analyzers the uncertainty caused by linearity can be brought down by calibrating the devices to a lower range. Here a range up to 500 ppb is used for calculations.

[‡] Noise at Zero for Thermo Scientific 450i calculated with a 60 s averaging time.

The devices are basically the same as the SO₂ analyzers assessed in the previous chapter as the H₂S is thermally converted to SO₂ (see chapter 3.1). Then the resulting SO₂ is analyzed using UV-fluorescence method which then directly corresponds to the H₂S concentration. The uncertainty constituents and effects are about the same with minor differences. Here also the largest contributor to both devices uncertainty is the one caused by linearity and also span drift (24h) with Thermo Scientific 450i.

With these calculations none of the Group 2 test concentrations (table 2.1) can be measured using an extended (k = 2.6) combined uncertainty to provide a 99 % confidence level and for Group 3 only the Serinus 55 is capable but only with a small headroom for gas concentration variations. If Battelle Class IV test from Others Group is discarded and the highest concentration to measure is about 100 ppb, then by using a range of up to 200

ppb would drop the extended uncertainty to 4 ppb for Serinus 55 and 6 ppb for Thermo Scientific. This would make the measurement of Group 3 H₂S concentration possible but Group 2 is still out of reach.

If suitable range can be selected and a suitable span gas can be found to use a range up to 100 ppb then Group 2 measurements can be done with extended uncertainties of 2.3 and 3.5 ppb for Serinus 55 and Thermo Scientific 450i respectively. This is especially important as noted in chapter 2.2.1 that the H₂S concentration is to be kept below 15-20 ppb to remain in Group 2 corrosive mechanics.

4.3 Nitrogen dioxide (NO₂)

Uncertainty analysis for Nitrogen dioxide analyzers Teledyne T500U and Ecotech Serinus 40 using Cavity Attenuated Phase Shift (chapt. 3.10) and chemiluminescence (chapt. 3.6) methods respectively is presented in table 4.4. As seen in table 2.1 the NO₂ concentrations are 200 ± 25 for every standard mentioned with slightly differing ranges. Calculations are done using a simulated reading of 225 ppb which should give the worst-case uncertainty for the analyzers.

Table 4.4: Uncertainty analysis and comparison of Teledyne T500U (Teledyne, 2016) and Ecotech Serinus 40 (Ecotech, 2018) NO₂ analyzers. All uncertainty constituents are uniformly distributed.

	Teledyne T500U Specification	u_c	Serinus 40 Specification	u_c
Range	0 - 5 ppb to 0 - 1 ppm		0 - 20 ppm autorang- ing	
Zero noise	< 20 ppt	0.01		
Span noise	< 0.2 % of reading + 0.02 ppt	0.27		
Zero drift	< 0.1 ppb / 24 hours	0.06	< 1.0 ppb / 7 days	0.23
Zero drift (temperature dependant)			0.1 ppb per °C	
Span drift	< 0.5 % of reading / 24 hours	0.65	< 1 % of reading / 7 days	1.30
Span drift (temperature dependant)			0.1 % per °C	
Linearity	< 1 % of full scale	5.77	± 1 % of full scale [†]	2.89
Precision	0.5 % of reading above 5 ppb	0.65	0.4 ppb otherwise 0.5 % of reading, whichever is greater	0.65
Combined		5.85		3.24
Extended (k=2.6)		15.22		8.42

[†] As with previous Serinus analyzers for SO₂ and H₂S the linearity error is based on the range and not the full scale. Range selected for calculations is 500 ppb.

With uncertainty calculations (table 4.4) based on an NO₂ concentration of 225 ppb the Teledyne T500U has an combined extended (k = 2.6) uncertainty of 16 ppb and Serinus 40 an combined extended (k = 2.6) uncertainty of 9 ppb both on an confidence level of 99 %. This means that both are capable of measuring an NO₂ concentration of 200 ± 25 with the Serinus 40 giving more headroom for gas concentration variations.

Largest contributor to both analyzers combined uncertainty is linearity. From table 4.4 for both the analyzers the effect of linearity is said to be below 1 % of full scale. According to an email conversation with Ecotech representative the effect of linearity in Serinus 40 is per range and can be calibrated to a lower range. This knowledge is used in the table. The same does not apply to Teledyne T500U.

The temperature dependant zero and span drift for Ecotech Serinus 40 can be mitigated by close regulation of air temperature surrounding the equipment. The other constituents cannot be really affected as they don't depend on anything that can be affected.

4.4 Chlorine (Cl₂)

Analyzers that measure parts-per-billion level chlorine gas in ambient air are very scarce as evidenced by subchapters regarding the measurement of chlorine, with many providers producing analyzers that measure Cl₂ from water - not air. The Honeywell SPM Flex analyzer which uses colorimetric Chemcassette-based (chapt. 3.3.1) detection offers trace-level chlorine measurement (Honeywell, 2016). No performance characteristics for uncertainty calculation are given in the operating manual nor specsheets or other material readily available from Honeywells website. The only mention of precision or accuracy comes from Technical Note 971131 (Honeywell, 2011) where they are unconventionally linked to "'true" values' and not the reading.

Table 4.5 shows uncertainty estimations based on the technical note. Based on this data Group 2 tests with 10 pbb Cl₂ concentration gives an extended uncertainty ($k = 2.6$) of 4 pbb on a confidence level of 99 % and Group 3 tests with 20 pbb Cl₂ gives an extended uncertainty ($k = 2.6$) of 8 pbb on a confidence level of 99 %. These values give no headroom for Cl₂ concentration variations as the ranges are $+0/-2$, ± 3 and ± 5 in the tests from table 2.1. Battelle Class IV is outright unmeasurable with its Cl₂ concentration of 50 ± 5 pbb as even the combined uncertainty is over the concentration limits.

Table 4.5: Uncertainty analysis of Honeywell SPM Flex Cl₂ analyzer (Honeywell, 2016). All uncertainty constituents are uniformly distributed.

	Honeywell SPM Flex Specification	u_c	u_c	u_c
Simulated reading		10	20	50
Accuracy	20-25 % of "true" value [†]	1.44	2.89	7.22
Precision	< 10 %	0.58	1.15	2.89
Combined		1.55	3.11	7.77
Extended $k=2.6$		4.04	8.08	20.21

[†] 25 % of reading used for uncertainty calculations.

5 Conclusion & Discussion

The different kinds of measuring methods for each gas are listed in chapter 3 that are based on the information from ASTM B827-05 (2014) and IEC 60068-2-60 (2015). On the basis of the information in the chapter and the uncertainty analysis in the chapter 4 the most suitable methods are:

- Ultraviolet Fluorescence for Sulfur Dioxide (SO₂).
- Ultraviolet Fluorescence for Hydrogen Sulfide (H₂S).
- Chemiluminescence or CAPS for Nitrogen dioxide (NO₂)
- Colorimetry based Chemcassette for Chlorine (Cl₂)

Of the measurement methods in chapter 3 some are outdated, too costly or have poor performance characteristics. UV-fluorescence spectroscopy and chemiluminescence seem like a clear choice above others as they are the standardized methods of ambient pollution monitoring. Why the other not quite suitable methods are included in the first place is a mystery to the author.

As explained in chapter 1.2 the uncertainty of an analyzer reduces the gas concentration variation headroom. Both the mass flow meter uncertainty and gas bottle concentration analysis uncertainty affect the gas concentration in the chamber. Thus an analyzer of better specifications makes the future gas dilution control process easier as the test gas has more room to vary in.

From the analyzers assessed the main source of uncertainty is the one caused by linearity except for the Chemcassette system which only lists accuracy and precision specifications. The uncertainty from linearity can be brought down by calibrating the devices to a lower range so long as it is suitable for the MFG test conditions. For detailed information see chapter 4.

Ecotech and Thermo Scientific list in their analyzers specifications that the linearity error is calculated of the full scale of the device. According to both manufacturers this was not the case and the linearity is really dependent on the selected range for which they are calibrated to. This piece of information was essential to get the uncertainties of the analyzers to a level suitable for MFG application. The distinction between range and full scale could have been explained more clearly in the manuals.

For the chemiluminescence method used to measure NO₂ concentration an interference of humidity on the measurement was found as described in chapter 3.6. Although uncertainty analysis for the Teledyne T500U has larger uncertainty than Serinus 40 it could prove to be better than the Serinus as it is not affected by humidity. Humidity also affects

the UV-fluorescence type SO₂ and H₂S analyzers as told in chapter 3.1. The quantization of the effect of humidity to the measurements has to be done to be sure of its effect on MFG test gas concentration levels.

References

- ABB (2017). *PGC5007*. url: https://library.e.abb.com/public/dbfdda2ddfc047aeaf5031c742451d6e/DS_PGC5007B-EN_A.pdf.
- Abbott, W.H. (1987). Corrosion of porous gold plating in field and laboratory environments. *Plat.Surf.Finish.*, 74(11), pp. 72–75.
- Abbott, W.H. (1988). The development and performance characteristics of mixed flowing gas test environment. *IEEE Transactions on Components, Hybrids, and Manufacturing Technology*, 11(1), pp. 22–35. doi:10.1109/33.2959. ID: 1.
- de Almeida, A. (2003). Energy-efficient motor systems in the industrial and in the services sectors in the European Union: characterisation, potential, barriers and policies. *Energy - The International Journal*, 28(7), pp. 67–90. url: <https://wilma.finna.fi/lut/PrimoRecord/pci.proquest27905733>.
- Arizona Instrument LLC (2017). *Jerome 631-X Hydrogen Sulfide Analyzer Operation Manual*. 3375 N Delaware Street, Chandler, AZ 85225 USA. url: https://www.azic.com/wp-content/uploads/2017/09/700-0037-F_MANUAL_631-X.pdf.
- Askew, W. (1989). DETERMINING CHLORINE CONCENTRATIONS IN AIR AND WATER SAMPLES FOR SCRUBBING STUDIES USING ION CHROMATOGRAPHY. *Journal of chromatographic science*, 27(1), pp. 42–46. url: <https://wilma.finna.fi/lut/PrimoRecord/pci.wosA1989R711100007>.
- Asmus, K.D., Gruenbein, W., and Fendler, J.H. (1970). Conductometric pulse radiolysis of sulfur hexafluoride in aqueous solutions. Rate of hydrolysis of sulfur tetrafluoride. *Journal of the American Chemical Society*, 92(9), pp. 2625–2628.
- ASTM (1976). *ASTM D 2912 : 1976 : R1983*. url: https://infostore.saiglobal.com/en-gb/Standards/ASTM-D-2912-76-R1983--143895_SAIG_ASTM_ASTM_319665/.
- ASTM B827-05 (2014). *Standard Practice for for Conducting Mixed Flowing Gas (MFG) Environmental Tests*. Standard. 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States: American Society for Testing and Material.
- ASTM B845-97 (2013). *Standard Guide for Mixed Flowing Gas (MFG) Tests for Electrical Contacts*. Standard. 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States: American Society for Testing and Material.
- Baglee, D., et al. (2017). How can SMEs adopt a new method to advanced maintenance strategies? A Case study approach.

- Bergamini, G., Bergamini, G., and Silvi, S. (2016). *Applied Photochemistry : When Light Meets Molecules*. Cham: Springer International Publishing. ISBN 9783319316710, Online resource p. Kuvailu Springer-palvelusta.
- Bluhme, A.B., Ingemar, J.L., Meusinger, C., and Johnson, M.S. (2016). Water vapor inhibits hydrogen sulfide detection in pulsed fluorescence sulfur monitors. *Atmospheric Measurement Techniques*, 9(6), pp. 2669–2673.
- Chromatotec (2006). *ChromaGC - CHROMATOTEC*. url: <http://www.chromatotec.com/Sulphur,compounds,analysis,H2S,COS,CS2,SO2,RSH,by,chromaS-Article-130-ChromaGC-Product-14.html>.
- Ecotech (2018). *Serinus 40 Oxides of Nitrogen Analyser - User Manual*. 1492 Ferntree Gully Road, Knoxfield, VIC Australia 3180: Author. url: <https://www.ecotech.com/wp-content/uploads/2018/07/ECOTECH-Serinus-40-NOx-User-Manual-3.3-M010028.pdf>.
- EIA 364-65B (2009). *MIXED FLOWING GAS TEST PROCEDURE FOR ELECTRICAL CONNECTORS CONTACTS AND SOCKETS*. Standard. 2500 Wilson Boulevard - suite 310, Arlington, VA 22201: Electronic Components Association.
- Honeywell (2011). *971131 Chemcassette-based Instrument Accuracy and Precision*. 405 Barclay Blvd. Lincolnshire, IL, 60069, USA: Author.
- Honeywell (2016). *SPM Flex Single Point Monitor Gas Detector User Manual*. 405 Barclay Boulevard, Lincolnshire, Illinois 60069, USA: Author.
- IEC 60068-2-60 (2015). *Environmental testing – Part 2-60: Tests – Test Ke: Flowing mixed gas corrosion test*. Standard. Geneva, CH: International Electrotechnical Commission.
- JCGM (2008). *JCGM 100: Evaluation of Measurement Data - Guide to the Expression of Uncertainty in Measurement*. Technical report. Joint Committee for Guides in Metrology.
- Kebabian, P.L., Robinson, W.A., and Freedman, A. (2007). Optical extinction monitor using cw cavity enhanced detection. *Review of Scientific Instruments*, 78(6), p. 063102. doi:10.1063/1.2744223, url: <https://doi.org/10.1063/1.2744223>. Doi: 10.1063/1.2744223; 19.
- Keco, A.S. (2015). *Laboratory H₂S Analyzer Series 150-Lab*. 9515 Windfern Rd, Houston, TX 77064: Author. url: <https://liquidgasanalyzers.com/wp-content/uploads/2014/10/150-Laboratory-H2S-Analyzer.pdf>.
- Kourtidis, K., Kelesis, A., and Petrakakis, M. (2008). *Hydrogen sulfide (H₂S) in urban ambient air*. url: <http://www.sciencedirect.com/science/article/>

- pii/S1352231008005797. doi://doi.org/10.1016/j.atmosenv.2008.05.066, ISBN 1352-2310. ID: 271798.
- Lakowicz, J.R. (2006). *Principles of Fluorescence Spectroscopy*, third edition edn. Boston, MA: Springer Science+Business Media, LLC. ISBN 9780387463124, verkkoaineisto: Springer p. Kuvailu Springer-palvelusta.
- Liptak, B.G. (2003). *Instrument Engineers' Handbook, Volume One: Process Measurement and Analysis*. CRC press.
- Liu, W. and Pecht, M. (2004). *IC component sockets*. Hoboken (NJ): Wiley-Interscience. ISBN 0-471-46050-8, 219 sivua p.
- Marta Doval Miñarro, E.G.F. (2012). Performance evaluation of two commercial chemiluminescence NO_x analysers according to European Standard EN 14211. *Journal of Environmental Monitoring*, 14(2), pp. 383–390.
- Matsumi, Y., Shigemori, H., and Takahashi, K. (2005). *Laser-induced fluorescence instrument for measuring atmospheric SO₂*. url: <http://www.sciencedirect.com/science/article/pii/S1352231005001664>. doi://doi.org/10.1016/j.atmosenv.2005.02.023, ISBN 1352-2310. ID: 271798.
- Millipore, E. (2015). *Reflectoquant System - brochure*. Billerica, MA, USA: Author. url: https://beta-static.fishersci.com/content/dam/fishersci/en_US/documents/programs/scientific/brochures-and-catalogs/brochures/emd-millipore-reflectoquant-brochure.pdf.
- Müller, H. (2000). *Sulfur Dioxide*. url: https://doi.org/10.1002/14356007.a25_569. doi:10.1002/14356007.a25_569, ISBN 9783-527306732.
- Nemoto Sensor Engineering Company Ltd (2016). *Technical Information and User Manual. NE4-CL" Electrochemical Chlorine (Cl₂) Gas Sensor*. 4-10-9 Takaido-Higashi, Suginami-ku, Tokyo 168-0072, Japan: Author. url: <http://www.nemoto.eu/assets/ne4-cl2-manual.pdf>.
- Nielsen, S.S. (2017). *Food Analysis*, 5th edn. Cham: Springer International Publishing. ISBN 9783319457765, Online resource p. Kuvailu Springer-palvelusta.
- Pouliquen, F., et al. (2000). *Hydrogen Sulfide*. url: https://doi.org/10.1002/14356007.a13_467. doi:10.1002/14356007.a13_467, ISBN 9783-527306732. .
- Ralfs, M. (1997). Disposable optochemical sensor for the determination of chlorine concentrations in the ppb-range. *Sensors & Actuators: B.Chemical*, 44(1-3), pp. 257–261. doi:10.1016/S0925-4005(97)00217-7, url: [https://wilma.finna.fi/lut/PrimoRecord/pci.sciversesciencedirect_elsevierS0925-4005\(97\)00217-7](https://wilma.finna.fi/lut/PrimoRecord/pci.sciversesciencedirect_elsevierS0925-4005(97)00217-7).

- Satterfield, Z. (2004). What does ppm or ppb mean? *On Tap*, 4(3), pp. 38–40.
- Schmittinger, P., et al. (2011). *Chlorine*. url: https://doi.org/10.1002/14356007.a06_399.pub3. doi:10.1002/14356007.a06_399.pub3, ISBN 9783-527306732. .
- Sick Maihak GmbH (2012). *MONOCOLOR IN and 2Ex Hydrogen Sulfide Gas Analyzer*. Nimburger Str. 11, 79276 Reute, Germany: Author. url: https://www.automationplus.it/docs/Sick/GAS/GAS\%20ESTRATTIVI/SICK_PI_MONOCOLOR_en_8009728_gasestrattivi.pdf.
- Symanski, J.S. and Bruckenstein, S. (1986). Conductometric sensor for parts per billion sulfur dioxide determination. *Analytical Chemistry*, 58(8), pp. 1771–1777.
- Telcordia GR-63-CORE (2012). *NEBSTM Requirements: Physical Protection*. Standard. One Telcordia Drive, Piscataway, NJ 08854: Telcordia Technologies, Inc.
- Teledyne (2016). *T500U*. url: <http://www.teledyne-api.com/products/nitrogen-compound-instruments/t500u>.
- Thiemann, M., Scheibler, E., and Wiegand, K.W. (2000). *Nitric Acid, Nitrous Acid, and Nitrogen Oxides*. url: https://doi.org/10.1002/14356007.a17_293. doi:10.1002/14356007.a17_293, ISBN 9783-527306732. .
- Urone, P., Evans, J.B., and Noyes, C.M. (1965). Tracer Techniques in Sulfur Dioxide-Air Pollution Studies. Apparatus and Studies of Sulfur Dioxide Colorimetric and Conductometric Methods. *Analytical Chemistry*, 37(9), pp. 1104–1107.
- Visamo, P. (2009). *Evaluating the measurement uncertainty for nitrogen oxides in air quality measurements*. Master's thesis. Lappeenranta University of Technology, Skinarilankatu 34, 53850 Lappeenranta, Finland.
- Vogel, G. (2016). *Creeping corrosion of copper on printed circuit board assemblies*. url: <http://www.sciencedirect.com/science/article/pii/S0026271416301871>. doi://doi.org/10.1016/j.microrel.2016.07.043, ISBN 0026-2714. ID: 271470.
- Vogel, G., Ag, S., and Amberg (2015). *Corrosive Gas Tests on Electronic Components and Modules in an industrial environment*. doi:10.13140/RG.2.2.34338.94408.
- Wrenn, C. (2014). *Application Note: 109. Getting the Most from Toxic Gas Sensors*. 1308 Continental Drive, Suite J, Abingdon, MD 21009: Environics USA, Inc. url: <https://www.environics.fi/wp-content/uploads/2014/06/ap-109-getting-the-most-from-toxic-gas-sensors-2014-02-05.pdf>.
- Zipp, A.P. and Evers, E.C. (1969). Conductometric behavior of sulfur-ammonia solutions. *Inorganic chemistry*, 8(8), pp. 1746–1748.