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Analytical Techniques for the determination of sulphur components in flue gas, fuel gas and natural gas

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**Literature thesis Chemistry,
Analytical Sciences**



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1 Introduction

The analyses of sulphur containing components in the different industrial gasses is a widely used measurement in the industrial environment. Sulphur is present in raw energy products when extracted from its sources for processing. Crude oils, raw coal and natural gas sources all contain sulphur in different concentrations and structure. Before crude oils are distilled in refineries or when coal is converted for the use of fuels, the sulphur is first removed from the raw feed streams. H₂S and in a lesser degree organic sulphur is formed during these conversion and treating steps. When natural gas is extracted from their sources the gas is treated in gas treating plants before use as an energy source in industries or households. The H₂S, COS and other organic sulphur in the gas are removed from the raw material. The importance of the removal of sulphur from the mentioned (energy) sources can be found in a number of reasons as the toxicity, corrosion and environmental pollution that will be caused by sulphur containing components.



Figure 1: Lemon yellow Sulphur crystals

The methods for the measurement of H₂S, COS and other organic sulphur are very broad. The analytical method used is first dependent on the range and composition of the gas. Second the analytical technology available at the time of choice plays a role in the selection. Over the last decades new analytical techniques are developed and have become available for the measurement of the sulphur containing components.

The emission of sulphur will be in the form of sulphur oxides after burning as SO₂ or SO₃ indicated as SO_x. The emission of the sulphur oxides among other pollutants is restricted in Europe. The European Union states: To maintain or improve the quality of ambient air, the European Union has established limit values for concentrations of sulphur dioxide, nitrogen dioxide and nitrogen oxides, particulate matter and lead, as well as alert thresholds for concentrations of sulphur dioxide and nitrogen oxide, in ambient air. The alert threshold laid down in Directive 1999/30/EC is 500 µg/m³ measured over three consecutive hours at locations representative of air quality over at least 100 km² or an entire zone or agglomeration, whichever is the smaller (1).

The emitted SO₂ by only the 25 European countries' industries was approximately 5,114,779 ton in 2004 (2004 data (2)), the power and refinery industry are the largest producers of SO₂.

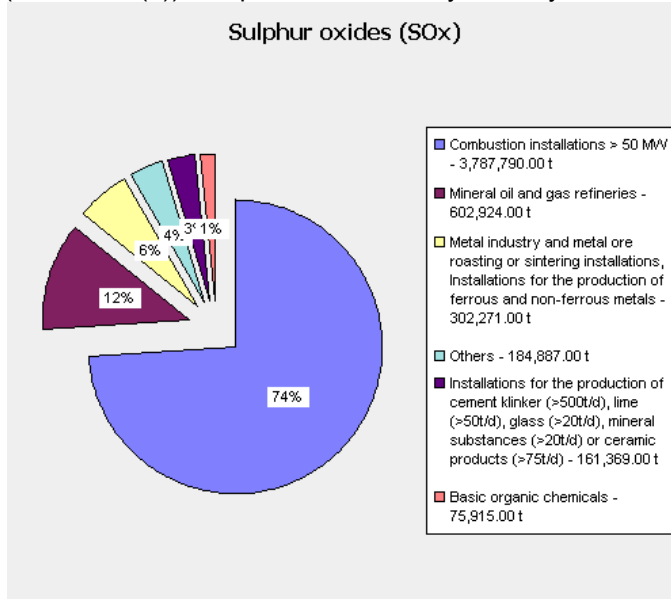


Figure 2: Emissions of SO₂ in 25 European countries in 2004 .

Therefore industrial companies have to restrict the amount of H₂S and other sulphur containing components exhausted to the incinerators and vented as SO₂ to the atmosphere. To control the emissions of the components analytical measurements are necessary. When regulations from governments limit the amount of pollutants, there must a way to measure and control this. This literature thesis will focus on the literature about the analyses of sulphur containing components and in particular SO₂, H₂S and COS in Flue gas, Fuel gas and Natural gas in a industrial environment.



Figure 3: Sulphur melts to a blood-red liquid. When burned, it emits a blue flame and forms SO₂ from: $S + O_2 \rightarrow SO_2$

2 Discussion of studied literature

The emission of SO_x in the EU-27⁽¹⁾ countries in Europe reported by the European Environment Agency (1) is displayed in Figure 4: Total EU-27 emission of SO_x (Gg).

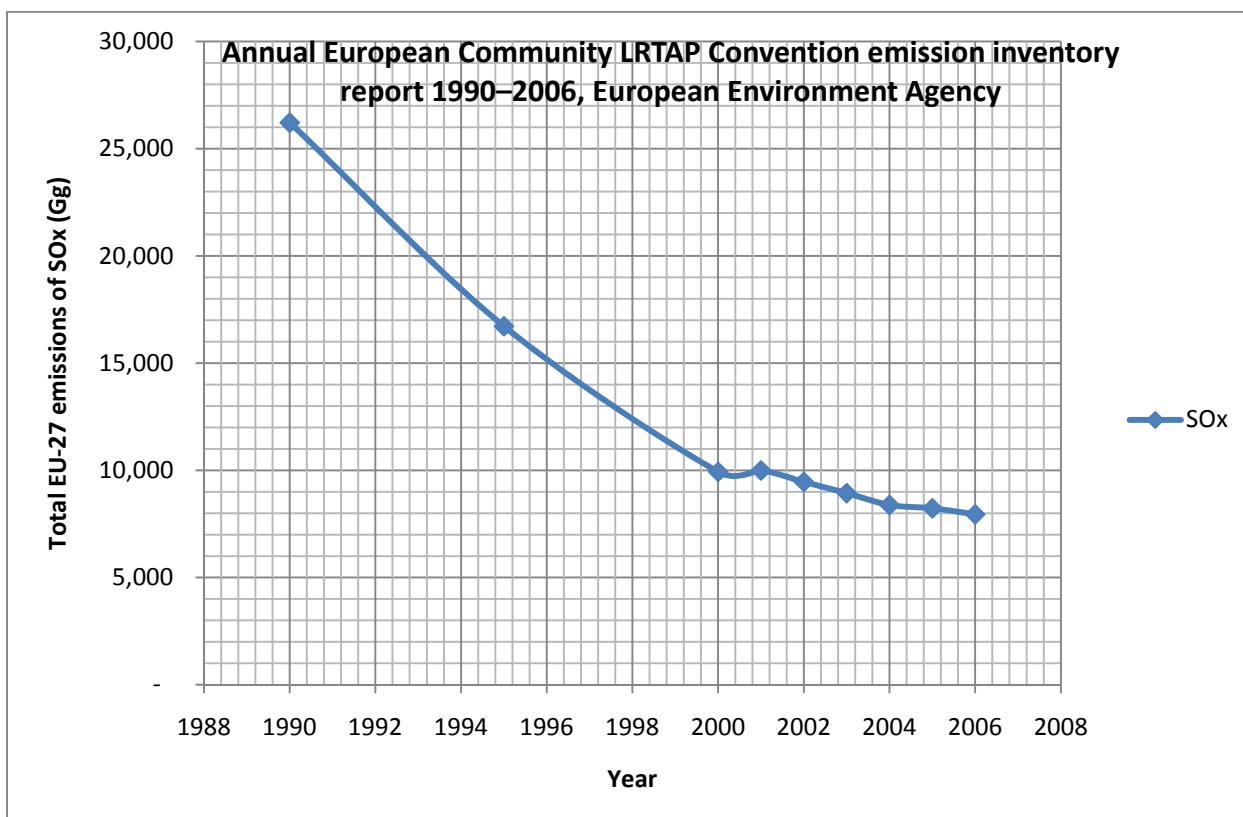


Figure 4: Total EU-27 emission of SO_x (Gg) Although the trend is down and the change was -70% from 1990 to 2006 and -3.4% from 2005 to 2006 still 7,946 Giga grams SO_x was released to the atmosphere in 2006 (1).

(1) EU-27: Austria, Belgium, Bulgaria, Cyprus, the Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, the Netherlands, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden and the United Kingdom.

2.1 SO_x emission trends (1):

The EU-27 total SO_x emissions in 2006 were 7,946 Gg. This is almost a 70% reduction compared to the level of emissions reported in 1990. Since 1990, SO_x emissions have increased in only two member states of the EU-27: Romania (21.9%) and Greece (11.9%). Inspection of the time-series trends for some member states of the EU-27 shows some step changes in emission reductions that have occurred since 1990. For example, emissions of SO_x in Slovenia fell considerably in 2001 and again in 2005 due to the introduction of flue gas desulphurisation equipment in thermal power plants. Between 2005 and 2006, the SO_x emission reduction in the EU was just over 3%, but five member states of the EU-27 reported increased emission, The highest increases in this last year were reported by Finland (more than 23%) and Denmark (almost 15 %) (Table 1). Figure 5 shows that emissions of SO_x from the two most important key categories in the EU-27 decreased between 2001 and 2006. SO_x emissions from public electricity and heat production, which accounts for more than 58% of total SO_x emissions, decreased by 2%. In the manufacturing industries and construction category (which accounts for 14% of total emissions) SO_x emissions decreased by 29% between 2000 and 2006. Emissions from the other key categories remained broadly constant between 2000 and 2006.

Table 1: Member States' contributions to European Community SO_x emissions (Gg)

	SO _x (Gg)										Change		Share in EU-27	
	1990	1995	2000	2001	2002	2003	2004	2005	2006	1990-2006	2005-2006	1990	2006	
Austria	74	47	32	33	32	32	27	27	28	- 62 %	6.8 %	0.3 %	0.4 %	
Belgium	354	262	171	169	158	154	157	144	139	- 61 %	- 3.4 %	1.4 %	1.7 %	
Bulgaria	1 517	1 300	1 045	1 096	965	968	929	900	877	- 42 %	- 2.6 %	5.8 %	11.0 %	
Cyprus	37	44	52	50	51	45	45	42	36	- 3 %	- 16.3 %	0.1 %	0.4 %	
Czech Republic	1 876	1 095	264	251	237	231	227	219	211	- 89 %	- 3.4 %	7.2 %	2.7 %	
Denmark	178	137	29	27	25	32	25	22	25	- 86 %	14.9 %	0.7 %	0.3 %	
Estonia	273	117	96	91	87	101	89	77	71	- 74 %	- 8.1 %	1.0 %	0.9 %	
Finland	259	95	89	85	79	99	84	69	85	- 67 %	23.1 %	1.0 %	1.1 %	
France	1 332	970	615	561	516	509	504	486	452	- 66 %	- 7.0 %	5.1 %	5.7 %	
Germany	5 353	1 724	637	641	601	605	582	574	558	- 90 %	- 2.6 %	20.4 %	7.0 %	
Greece	487	536	493	502	513	545	529	545	536	12 %	- 1.7 %	1.9 %	6.7 %	
Hungary	1 010	707	489	404	365	347	248	129	118	- 88 %	- 8.5 %	3.9 %	1.5 %	
Ireland	183	160	137	129	99	78	72	71	60	- 67 %	- 15.6 %	0.7 %	0.8 %	
Italy	1 794	1 320	755	704	622	525	488	408	389	- 78 %	- 4.7 %	6.8 %	4.9 %	
Latvia	101	48	10	8	6	5	4	4	3	- 97 %	- 9.9 %	0.4 %	0.0 %	
Lithuania	214	85	42	38	43	43	42	44	43	- 80 %	- 2.0 %	0.8 %	0.5 %	
Luxembourg	14	6	1.3	1.4	1.3	1.2	1.2	1.1	0.04	- 100 %	- 96.5 %	0.1 %	0.0 %	
Malta	16	29	24	26	25	27	12	12	12	- 21 %	0.9 %	0.1 %	0.2 %	
Netherlands	190	128	72	73	66	63	65	65	64	- 66 %	- 2.4 %	0.7 %	0.8 %	
Poland	3 210	2 376	1 202	1 564	1 455	1 375	1 241	1 222	1 195	- 63 %	- 2.2 %	12.2 %	15.0 %	
Portugal	320	334	307	296	296	202	214	214	191	- 40 %	- 10.8 %	1.2 %	2.4 %	
Romania	707	619	439	469	484	493	479	831	863	22 %	3.8 %	2.7 %	10.9 %	
Slovakia	526	246	127	131	103	106	97	89	88	- 83 %	- 1.4 %	2.0 %	1.1 %	
Slovenia	198	126	99	69	71	66	54	41	18	- 91 %	- 56.5 %	0.8 %	0.2 %	
Spain	2 169	1 786	1 458	1 433	1 536	1 270	1 312	1 264	1 170	- 46 %	- 7.5 %	8.3 %	14.7 %	
Sweden	108	71	46	44	45	45	41	40	39	- 64 %	- 0.7 %	0.4 %	0.5 %	
United Kingdom	3 717	2 352	1 198	1 095	978	967	812	688	676	- 82 %	- 1.8 %	14.2 %	8.5 %	
EU-27	26 217	16 719	9 928	9 992	9 460	8 935	8 382	8 227	7 946	- 70 %	- 3.4 %	100 %	100 %	

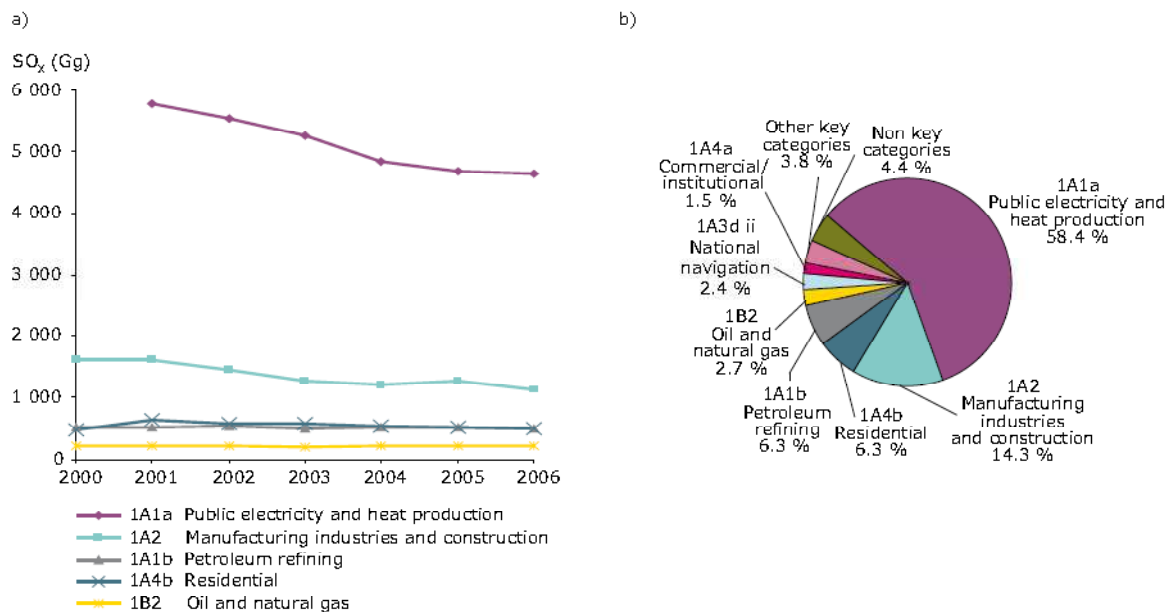


Figure 5: SO_x emissions from key categories in EU-27: (a) Trend in SO_x emissions from the five most important key categories, 1990–2006; (b) Contribution of key categories to SO_x emissions, 2006

Natural sources of SO₂ include releases from volcanoes, oceans, biological decay and forest fires. Actual amounts released from natural sources in the world are difficult to quantify; in 1983 the United Nations Environment Programme estimated a figure of between 80 million and 288 million tonnes of sulphur oxides per year. Man-made sulphur dioxide emissions result from combustion or burning of fossil fuels, due to varying amounts of sulphur being present in these fuels. Worldwide emissions of SO₂ are thought to be around 69 million tonnes per year (3).

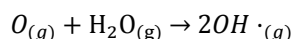
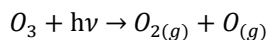
SO₂ is formed during the combustion of fuels, the sulphur is oxidised to sulphur dioxide by: $S + O_2 \Rightarrow SO_2$. The Sulphur content in fuels is distributed as displayed in Table 2. Coal and fuel oils have the largest content of sulphur.

Table 2: Sulphur contents of fuels (4).

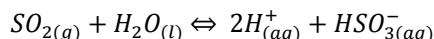
Fuel	S (% by weight)
Coal	7.0-0.2
Fuel oils	4.0-0.5
Coke	2.5-1.5
Diesel fuel	0.9-0.3
Petrol	0.1
Kerosene	0.1
Wood	very small
Natural gas	very small

The SO₂ will be present in the atmosphere as it is released by the different mentioned sources. Mixing times in the atmosphere is very fast. For example the nuclear reactor accident in 1986 could be quickly detected all over the globe. Pollutants particles from Europe and North America can be detected over China. This mixing will also dilute the contaminants (4). The SO₂ will react in the Troposphere, the first

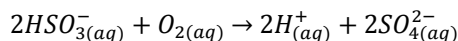
20km of atmosphere. The most important reactive entity in that atmosphere is the hydroxyl (OH·) radical. It is formed in the atmosphere by the photochemically initiated reaction sequence of O₃ (ozone) with a photon hν. Water in the atmosphere will react with the atomic oxygen to form a hydroxyl radical.



The hydroxyl radicals can react with the pollutants present in the atmosphere (e.g. 2OH· + SO₂ -> H₂SO₄). If a pollutant has a fast rate of reaction with the hydroxyl radicals its residence time is short e.g. SO₂ has a residence time of 3-7 days. Sulphuric acid (H₂SO₄) is formed and dissolved in H₂O will eventually fall back to the earth in the form of acid rain (pH 2-3). The classical example is that of the air pollution accident in London during winter in 1952 under foggy and damp conditions (4). Fuel use was at its highest and air near-stagnant. Sulphur is fairly soluble so could dissolve into the water that condensed around smoke particles. (The so called smog= sm[oke] + f[og])



Traces of metal contaminants (iron (Fe) or manganese (Mn)) catalysed the conversion of dissolved SO₂ to H₂SO₄.



The sulphuric acid has a great affinity for water so the droplet absorbed more water. Gradually the droplets grew and formed the acid rain. The sulphuric acid is a very powerful corrosion agent and rust iron bars and weathers building stones. The mentioned air pollution accident in London during winter in 1952 resulted in a great number of deaths. The graph in Figure 6 shows the relation between the concentration SO₂ and the deaths at that period (3).

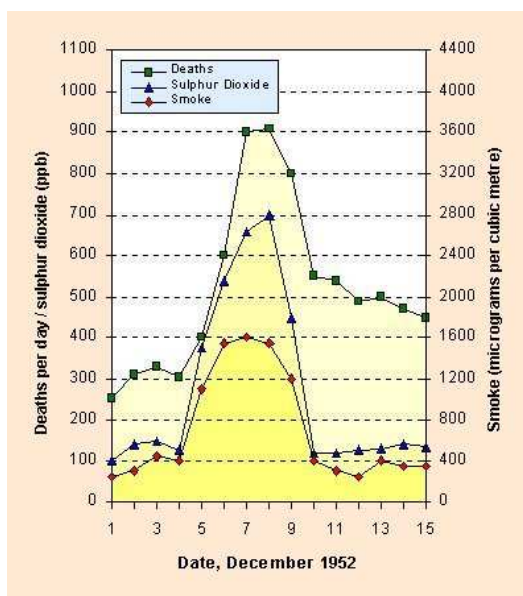


Figure 6: The London smog deaths in December, 1952 (3)

Since that time a lot of effort has been put in the reduction of emission of sulphur to the atmosphere. Dictated by the governments several programmes have been released. E.g. for the reduction of pollutions the United Nations Economic Commission for Europe (UNECE), of which the European countries, the European Commission, the United States and Canada are members, have signed the 1999 Gothenburg Protocol. For SO_2 this protocol dictates an emission limit per country. For The Netherlands this limit is set to a maximum of 50ktons in 2010 (5).

Another aspect of sulphur species and particular H_2S is its toxicity. First the toxicity toward live. H_2S for example is toxic to human beings. H_2S is classed as a chemical asphyxiant, similar to carbon monoxide and cyanide gases. It inhibits cellular respiration and uptake of oxygen, causing biochemical suffocation.

Typical exposure symptoms include:

- 0 - 10 ppm Irritation of the eyes, nose and throat,
- 10 - 50 ppm Headache, dizziness, nausea and vomiting, coughing and breathing difficulty
- 50 - 200 ppm Severe respiratory tract irritation, eye irritation / acute conjunctivitis, shock, convulsions coma, death in severe cases

Prolonged exposures at lower levels can lead to bronchitis, pneumonia, migraine headaches, pulmonary oedema, and loss of motor coordination. H_2S will anaesthetize the smell sense organs at levels of 10ppm and higher.

H_2S and COS has a negative effect on catalyst, while it degrades its functionality and activity or corrosion of steel material.

2.2 The Industries

The two industries responsible for the largest emission of SO_2 are the Power plants and Refinery industries, since they make use of coal and fuel oils. Coal has a content of between 7.0-0.2% sulphur and oil between 4.0-0.5% sulphur (ref Table 2). During the burning at the high temperatures with oxygen concentrations typical of combustion, sulphur combines with carbon, hydrogen and oxygen to form SO_2 , SO_3 , SO , CS , CH , COS , H_2S , S and S_2 (6).

2.2.1 Power plants:

In the EU-15 (15 European countries) approximately 1361 large power plants sites exists. For those processes using coal and fuel oils as fuel for combustion as in power plants a number of sulphur removal processes are available and are used to remove the sulphur from the flue gas. First these are primary measures to reduce sulphur oxide emissions by low sulphur fuels or the use of absorbents in fluidised bed combustion systems (the adsorbent used is usually CaO , $\text{Ca}(\text{OH})_2$ or CaCO_3). Then secondary measures to reduce sulphur oxide emissions are available (6).



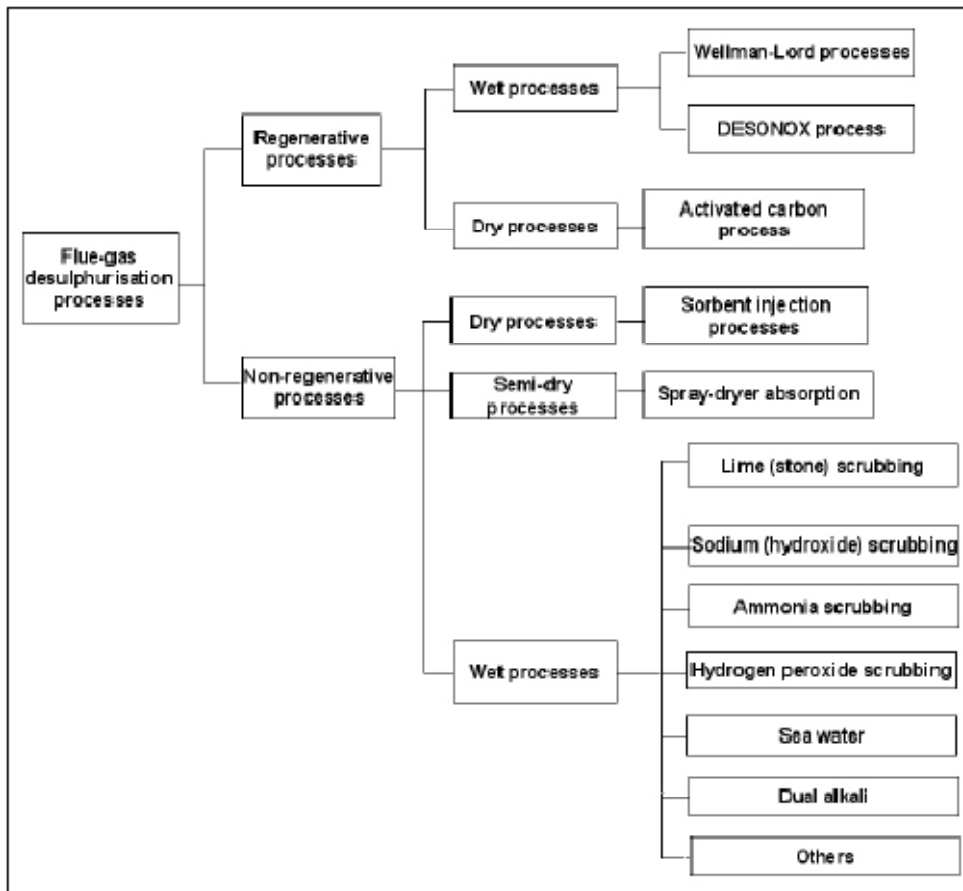


Figure 7: The common flue-gas desulphurisation (FGD) technologies to reduce sulphur oxide emissions (secondary systems)

Wet scrubbers, especially the limestone-gypsum processes, are the leading flue-gas desulphurisation (FGD) technologies. They have about 80% of the market share and are used in large utility boilers. This is due to their high SO₂ removal efficiency and their high reliability. Limestone is used in most cases as the sorbent, as it is available in large amounts in many countries and is cheaper to process than other sorbents. By-products are either gypsum or a mixture of calcium sulphate/sulphite, depending on the oxidation mode. If the gypsum can be sold, total overall operating costs may be reduced (6).

In the worldwide hierarchy of applied FGD systems, spray dry scrubbers have the second place behind wet scrubbers. Lime slurry is usually used to remove SO₂ from the flue-gas in this type of FGD.

In regenerable processes the spent sorbent is re-used after thermal or chemical treatment to produce concentrated SO₂ which then usually is converted to elemental sulphur by the sulphur recovery plant (6).

2.2.2 Refineries:

There are currently around hundred crude oil refineries spread around the EU countries. In these refineries the crude oil is treated by one of the largest systems for the removal of H₂S produced across the refinery. These systems typically contain an amine scrubbing system and a sulphur recovery unit to convert H₂S into sulphur. The gasses with a H₂S content of over 25% can be treated by the Claus process, this is the most significant gas desulphurisation processes, recovering elemental sulphur from H₂S (6). Sulphur management within a refinery consist of four basic processes. Amine treating units to

(ATUs) remove H₂S from recycle gas streams in hydro-processing operations and from fuel gas/liquefied petroleum gas (LPG) recovery units. The amine is regenerated in one or more amine regeneration units (ARUs). Sour water strippers (SWSs) to remove H₂S and NH₃ from the steam used in steam distillation (called sour water). The sulphur in the acid gas from the amine recovery unit and the sour water stripper is removed first by the Claus sulphur recovery unit (SRU). 92-96% of the sulphur is recovered here. Then in a second step, the tail gas clean up unit, the overall sulphur recovery can be increased to 99.9%. Also the refineries degas the molten sulphur (7).

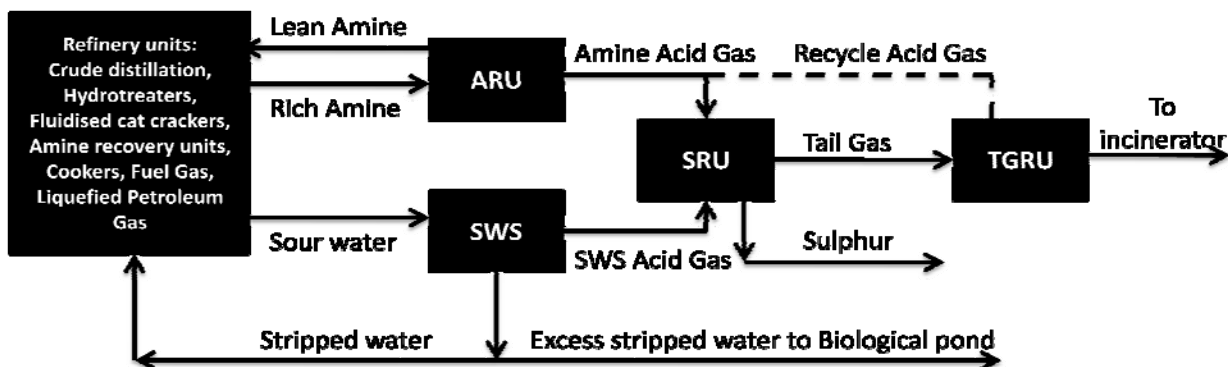


Figure 8: Sulphur Removal / Recovery in a refinery (7)

In the Claus Process the H₂S is converted in two steps (7):

1. The Thermal step: The H₂S is partially oxidised with air at a high temperature (1000-1400°C). Sulphur is formed, but some H₂S remains un-reacted and some SO₂ is formed.

The reaction:
$$2H_2S + 3O_2 \Rightarrow 2SO_2 + 2H_2O$$

2. The Catalytic step: The remaining H₂S is reacted with SO₂ at a lower temperatures (200-300°C) over a catalyst to sulphur. More catalytic stages are needed to get a higher efficiency.

The reaction:
$$2H_2S + SO_2 \Rightarrow 3S + 2H_2O$$

To increase efficiency a number of improvements have been developed over the last decades. The Superclaus^(TM) process, which uses a special catalyst in last stage to get to an higher efficiency of 99.9% or a oxygen Claus unit, which used pure oxygen to get a higher throughput.

2.2.3 Natural gas:

In natural gas sulphur exists mainly in the form of H_2S . Small amounts of COS and mercaptanes exist but H_2S is the largest contaminant. The gas is called sour if more than approximately 5.7 milligrams of H_2S per m^3 natural gas is present. The process for the removal of H_2S from natural gas is called the sweetening of the gas. The main process for the removal of H_2S from natural gas is the amine treating unit and a Claus sulphur recovery unit.

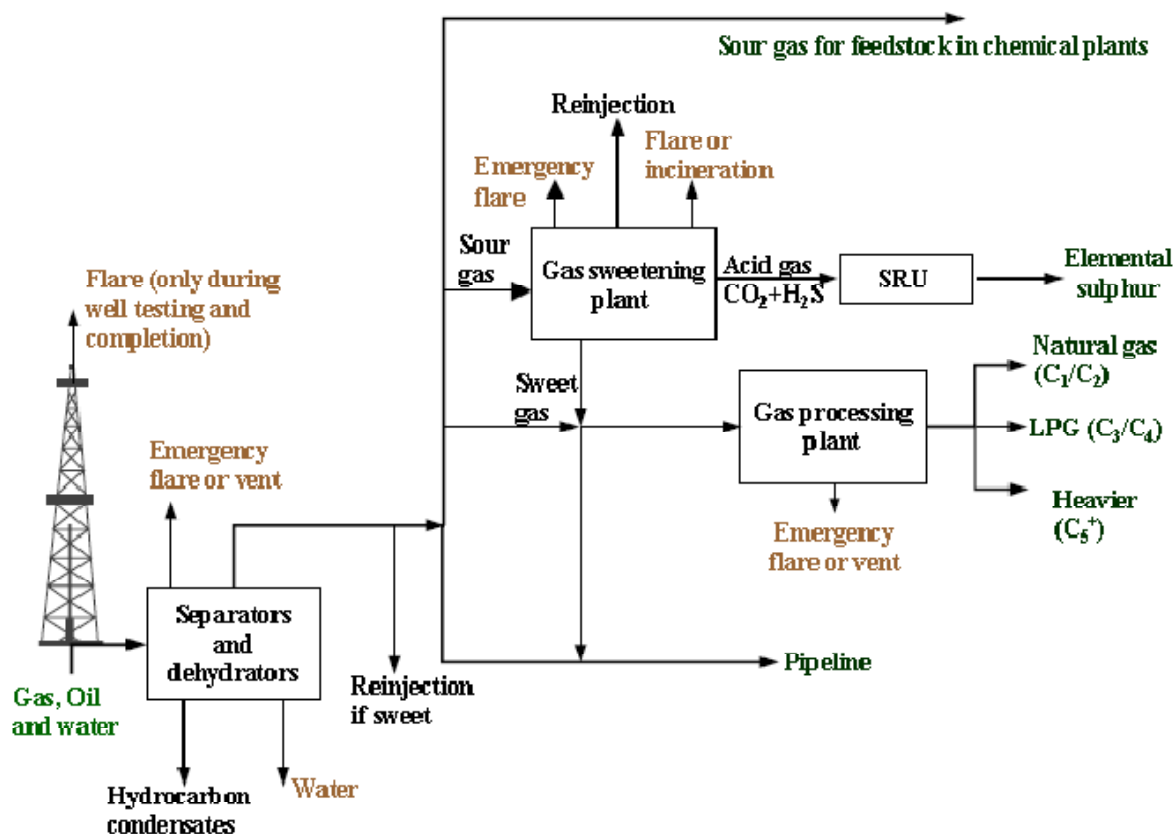


Figure 9: Natural gas plant and treating

2.3 The analyses of H_2S and other sulphur containing components in gasses

When SO_2 is released to the atmosphere or when the treating steps, to remove sulphur in the form of H_2S , are executed the components must be measured in order to register the emissions. The analyses of the SO_2 and H_2S are performed to quantify the amount of pollutant released to the atmosphere. During, and in between the treating steps the quantification of treated gas and its impurities is performed to control and monitor the processes in which the treating takes place.

The literature describes a great deal of instrumentation that could be used for the measurement of the sulphur pollutants. Instead of reviewing all the types and instruments the focus will be on the instrumentation that is most suitable for the applications of interest. First an overview is given about the amount of SO_2 , H_2S and total sulphur that is present in the products and the application of interest vs the analytical technique available.

2.3.1 Emission levels

The maximum concentration levels allowed from 2008 as dictated by the European Union, USA EPA, and China is displayed in Table 3. The concentrations in Table 3 will dictate the measuring range for the analytical equipment.

Table 3: Maximum emission levels of Sulphur components in Europe, USA and China (2)

Max levels	SO ₂	H ₂ S	Total S ULS/LS ^(*)
Flue gas	500ug/m3 72h/m3 EU 365ug/m3 24h USA	5-10ppm	-
Natural gas	-	3 ppm EU 4.2 ppm USA	120ppm EU (8)
Fuel gas	-	2500ppm	-
Diesel & Fuels	-	-	10/50ppm EU 15/500ppm USA 500-2000ppm China

(*)ULS=Ultra Low Sulphur, LS=Low Sulphur

2.3.2 Analytical techniques

An overview of analytical techniques available for H₂S and SO₂ in Flue gas, Fuel gas and Natural gas and Total Sulphur are displayed in Table 4. The dynamic range for the analytical equipment that will dictate if the specific technique can be used for the intended application is displayed in Table 5Table 4.

Table 4: Analytical techniques available for H₂S, SO₂ and Total Sulphur in Flue gas, Fuel gas and Natural gas

Application vs Analytical Technique	Lead acetate paper tape	UV Spectroscopy	FPD/PFPD Gas-chromatographic	µTCD Gas-chromatographic	TCD/DMD µGas-chromatographic	Chemiluminescence	X-Ray spectroscopy	Photo ionisation	Titrimetric	Conductimetric	Diode array spectroscopy	Tunable Diode Laser (TDL-method)	Cavity Ring-Down Spectroscopy (CRDS)
SO ₂ in Flue gas		X	X	X	X	X					X		
H ₂ S in Flue gas	X	X	X	X	X	X		X	X	X	X	X	X
H ₂ S in Fuel gas	X	X	X	X	X			X	X	X	X	X	X
H ₂ S in Natural gas	X	X	X	X	X			X	X	X	X	X	X
Total Sulphur	X		X	X	X		X				X		

2.3.3 The dynamic ranges & detection limits (LOD)

Table 5: Analyser Technique vs Ranges & LOD for H₂S and SO₂ in Gasses

Application vs Analytical Technique (Range/ Detection limit)	Lead acetate paper tape (9) (10)	UV Spectro - photometry (11)	FPD/PFPD Gas- chromatographic (12)	µTCD Gas- chromatographic (13)	DMD Gas- chromatographic (14) (15)	Chemiluminescence/ AED (12)	X-Ray spectroscopy (16)
SO ₂ in Flue gas		0-25ppm 0-250ppm 100ppb LOD	50ppb-100ppm 10ppb-100ppm 10ppb LOD	0.5ppm-% 0.5ppm LOD	200ppb- 10ppm 200ppb LOD	5ppb-1% 5ppb LOD	
H ₂ S in Flue gas	0.010ppm-% 10ppb LOD	0-5ppm 100ppb LOD	50ppb-100ppm 10ppb-100ppm 10ppb LOD	0.5ppm-% 0.5ppm LOD	200ppb- 10ppm 200ppb LOD	5ppb-1% 5ppb LOD	
H ₂ S in Fuel gas	0.010ppm-% 10ppb LOD	0-5ppm 100ppb LOD	50ppb-100ppm 10ppb-100ppm 10ppb LOD	0.5ppm-% 0.5ppm LOD	200ppb- 10ppm 200ppb LOD		
H ₂ S in Natural gas	0.010ppm-% 10ppb LOD	0-5ppm 100ppb LOD	50ppb-100ppm 10ppb-100ppm 10ppb LOD	0.5ppm-% 0.5ppm LOD	200ppb- 10ppm 200ppb LOD		
Total Sulphur	0.010ppm-% 10ppb LOD		200ppb- 500ppm 40ppb-500ppm 40ppb LOD	0.5ppm-% 0.5ppm LOD	200ppb- 40ppm 200ppb LOD		1ppm-% 1ppm LOD
Application vs Analytical Technique (Range/ Detection limit)	Photo ionisation (17)	Titrimetric (17)	Conductimetric (17)	Diode array spectroscopy (18)	Tunable Diode Laser (TDL-method) (11)	Cavity Ring-Down Spectroscopy (CRDS) (19)	
SO ₂ in Flue gas				0-500ppm			
H ₂ S in Flue gas	0.1-1500ppm 100ppb LOD	0-1ppm 0-1000ppm	0-2ppm 0-750ppm	0-10ppm ppm-%	0-20ppm 500ppb	0-1000ppm 200ppb	
H ₂ S in Fuel gas	0.1-1500ppm 100ppb LOD	0-1ppm 0-1000ppm	0-2ppm 0-750ppm	0-10ppm ppm-%	0-20ppm 500ppb	0-1000ppm 200ppb	
H ₂ S in Natural gas	0.1-1500ppm 100ppb LOD	0-1ppm 0-1000ppm	0-2ppm 0-750ppm	0-10ppm ppm-%	0-20ppm 500ppb	0-1000ppm 200ppb	
Total Sulphur				0-10ppm			



2.3.4 Repeatability

Table 6 displays the repeatability data of different analytical techniques for determination of SO₂, H₂S and Total Sulphur. The repeatability is defined as the difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material (20).

Table 6: General repeatability data (%RSD) for the different techniques

Application vs Analytical Technique Repeatability %RSD	Lead acetate paper tape (20)	UV Spectro photometry (11)	FPD/PPFD Gas-chromatographic (21)	μTCD Gas-chromatographic (14)	DMD Gas-chromatographic (14)	Chemiluminescence (22)	X-Ray spectroscopy (17)	Photo ionisation (17)	Titrimetric (17)	Conductimetric (17)	Diode array spectroscopy (18)	Tunable Diode Laser (TDL-method) (11)	Cavity Ring-Down (19) Spectroscopy (CRDS)
SO ₂ in Flue gas		2%	2%	1%	3%	5%					1%		
H ₂ S in Flue gas	10%	2%	2%	1%	3%	5%		2%	4%	6%	1%	2-5%	-
H ₂ S in Fuel gas		2%	2%	1%	3%			2%	4%	6%	1%	2-5%	-
H ₂ S in Natural gas		2%	2%	1%	3%			2%	4%	6%	1%	2-5%	-
Total Sulphur	10%		2%	1%	3%		2-13%				1%		

2.3.5 Analytical speed

Table 7 displays the analytical speed of the different analytical techniques for determination of SO₂, H₂S and Total Sulphur.

Table 7: Typical analytical speeds for the different techniques

Application vs Analytical Technique	Lead acetate paper tape (20)	UV Spectro photometry (11)	FPD/PFPD Gas-chromatographic (21)	μTCD Gas-chromatographic (14)	DMD Gas-chromatographic (14)	Chemiluminescence (22)	X-Ray spectroscopy (17)	Photo ionisation (23)	Titrimetric (**) (17)	Conductimetric (17)	Diode array spectroscopy (18)	Tunable Diode Laser (TDL-method) (11)	Cavity Ring-Down (19) Spectroscopy (CRDS)
SO ₂ in Flue gas		<30s	180s	30-60s	30-60s	180s					10-20s		
H ₂ S in Flue gas	180s	<30s	180s	30-60s	30-60s	180s		5s	300s	200s	10-20s	<60s	-
H ₂ S in Fuel gas		<30s	180s	30-60s	30-60s	180s		5s	300s	200s	10-20s	<60s	-
H ₂ S in Natural gas		<30s	180s	30-60s	30-60s	180s		5s	300s	200s	10-20s	<60s	-
Total Sulphur	180s		720s	180s	180s	720s	200s-600s				20s		

(*)The mentioned analytical speeds are excluded sample times from the sample take off point and sample handling system.

(**) Analyses time is estimated.

2.3.6 Gas Chromatography (GC)

A great deal of literature describes the measurement of sulphur components with gas-chromatographic methods (24) (15) (17) (25) (9) (26) (27) (12) (28) (29). Gas chromatography has the advantage to measure the components of interest in a compositional background. It will first separate the components of interest from the bulk composition in a separation column and then leads the components over a detector. The separation column for the measurement of sulphur components can be chosen in packed and capillary type. For combinations of low quantity detection and specific detectors ({Pulsed} Flame Photometric Detector (FPD/PFPD), Chemiluminescence Detector) packed column allow a higher injection volume than capillary columns and are therefore chosen. Specific detectors have the advantage that the bulk composition remains undetected and therefore has less interfering effects than universal detectors. Total sulphur in the gas phase may be determined measuring a number of individual sulphur components and adding up the total or first converting all present sulphur species to SO₂ and reporting the total sulphur as SO₂ concentration (28). Total sulphur in diesel and liquid fuels is available using the gas chromatographic techniques (13) (22) (28). The sulphur is either oxidized in an oven at 800-1000°C to SO₂ and separated by a chromatographic column and detected on a FPD (28) or the sample is injected and vaporized and the individual sulphur components are separated and detected by a sulphur selective detector (13) (30).



An overview is given in the literature about a comparison of Sulphur Selective Detectors for low level analyses in gaseous streams (30).

Table 8: A comparison between 4 detectors (FPD, PFPD, SCD, AED) (30)

Detector characteristics				
Detector ^(*)	FPD	PFPD	SCD	AED
Supplier	Agilent	OI	Sievers/Antek	Agilent
MDL Sulphur [pg/sec]	20	1	0.5	2
Selectivity	10 ⁵	10 ⁶	10 ⁶	10 ⁵
Dynamic range	10 ³	10 ³	10 ⁵	10 ⁴
Quenching	Yes	Yes	No	No
Equimolar response	Approximate	Yes	Yes	Yes
Packed Column compatible	Yes	No, 1ml/min flow	Yes	Yes
Other elements detectable	P, Sn	P	N	C,H,N,O,Cl,etc total 26
Approximate relative costs	\$	\$\$	\$\$\$	\$\$\$\$
Detection limit S [ppbv]	50	10	5	5

^{*}(FPD = Flame Photometric Detector, PFPD = Pulsed Flame Photometric Detector, SCD =, Sulphur Chemiluminescent Detector, AED = Atomic Emission Detector)

With the gas-chromatographic technique, using a FPD and the total oxidation of sulphur to SO₂, quantification of 5.16ppm total sulphur with 0.13ppm standard deviation could be achieved. With the techniques it is critical that all components, including sample tubing and sample system components which come in contact with the sample are Silco coated steel, Teflon, or quartz. Dead volumes in the system must be minimized to eliminate sample contamination between sample injects (28).

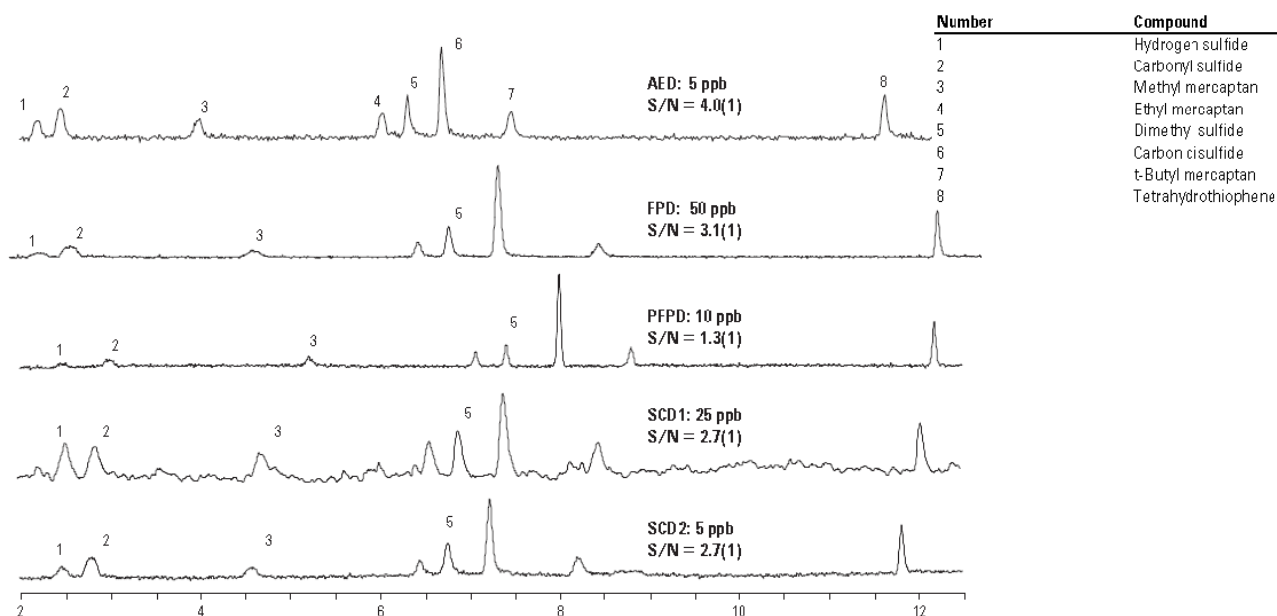


Figure 10: Detection limits for four sulphur selective detectors using an eight component calibration mix

New developments over the last decade allow the detection of sulphur using new detectors. As discussed in (15) and (14) the detection of SO₂, H₂S, COS and CH₃SH in a range from 200ppbv to 5ppmv in hydrocarbon gasses could be achieved using a μGC in combination with a CP-Sil5 column and a micro-Differential Mobility Detector (μDMD). In combination with the micro-Thermal Conductivity Detector (μTCD) and a Pora PLOT U column quantification limits of 0.5 ppm H₂S in Natural Gas could be achieved with a 2-8% repeatability in the 1-3ppm H₂S range.

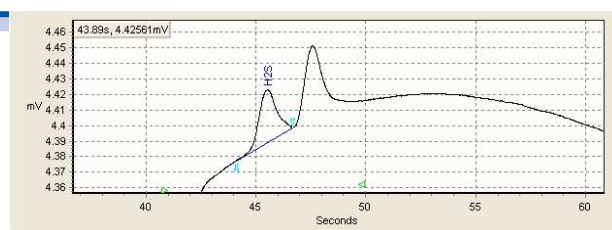
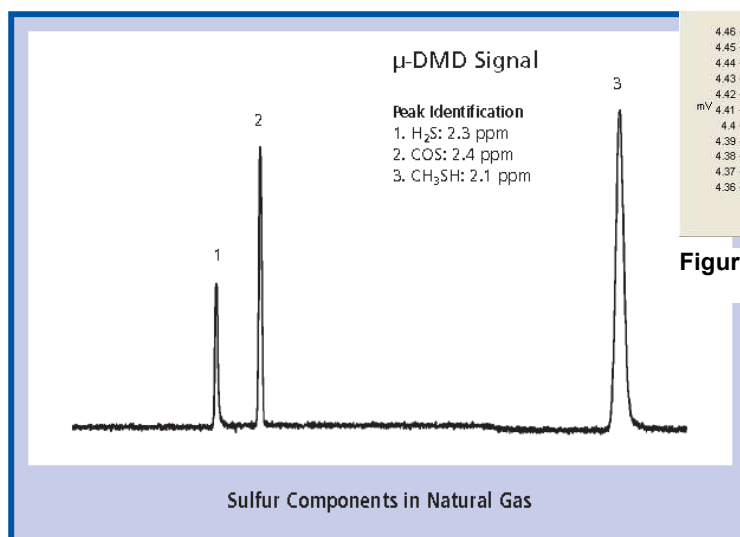


Figure 11: 5.8ppmv H₂S LOQ 0.5 ppmv on a μTCD

Figure 12: μDMD chromatogram for H₂S, COS and CH₃SH (detection limits 200ppbv)

Table 9: Repeatability for 1-3ppm H₂S on a μTCD (31)

H ₂ S Conc	%RSD
3ppm	2-3%
2ppm	3-4%
1ppm	8%

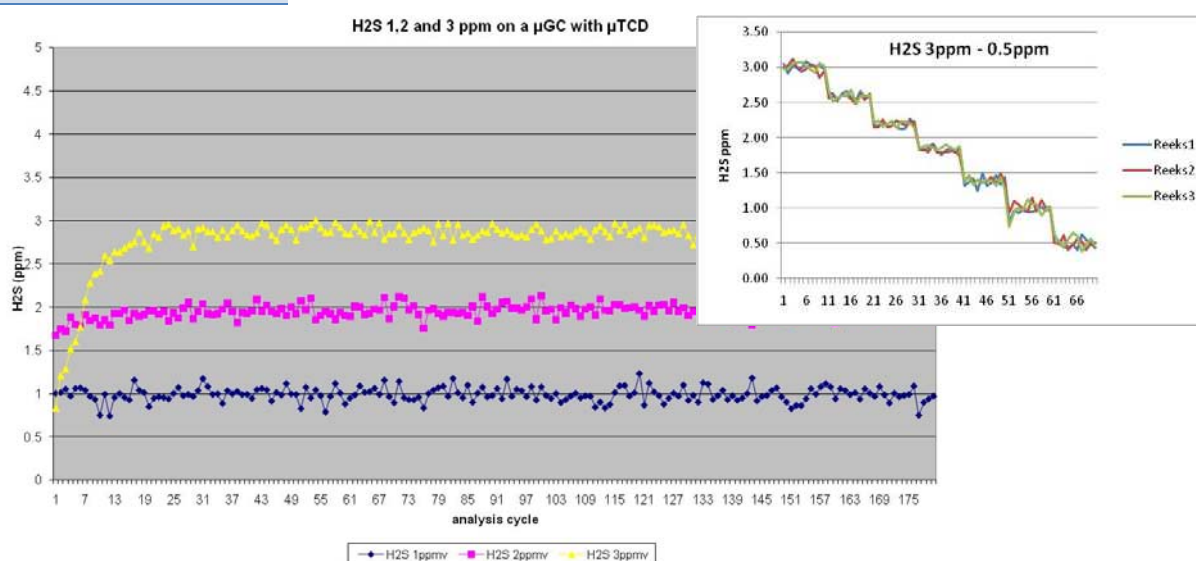
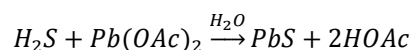


Figure 13: Stability and step test for 3 to 0.5ppm H₂S on a μTCD

2.3.7 Lead acetate tape technology

Lead acetate tape technology is a technique using a paper or cloth tape (white in colour) that is saturated with a lead acetate solution, dried, then spooled similar to a tape recorder. The gas sample is moistened as it flows through a humidifier, then passes over or through the tape in a small, confined area, typically 1/8" in diameter. The portion of the tape exposed to the sample gas stream will darken proportionally to the amount of H₂S present, due to the formation of lead sulphide.



$$\text{Change of colour} = \text{Constant} \times [H_2S]$$

Since the lead sulphide is coloured, and the lead acetate and paper tape are not, the rate of formation of lead sulphide may be determined by measuring the rate of darkening of the tape. The degree of stain, or the colour of the stain are not important; only the rate at which the stain occurs. The tape will gradually be transported in the sample gas stream which allows a semi-continuous measurement of the sulphur components in a range of 0.01ppm to percentage level (10).

The analyser system is negatively influenced by temperature fluctuations due to the fluctuations in tape humidification and sample pressure fluctuations (25), which will lead to a changes in the colour intensity and misreading of the instrument. In some cases this will lead to tape breakage due to over humidification of the tape. Some manufacturers use a derivative of the colour and measure the colour change instead of the absolute colour and report concentrations as a rate of change of colour. The cycle time to perform one analysis is 180sec. The system has a number of ASTM (20) approvals (ref. Appendix 1: ASTM (American Standard Test Methods)), which makes the measurement reproducible, comparable and traceable.

The ASTM D4084-07 dictates the precision of the instrument used. The data displayed in Figure 14 should be used to judge acceptability of test results:

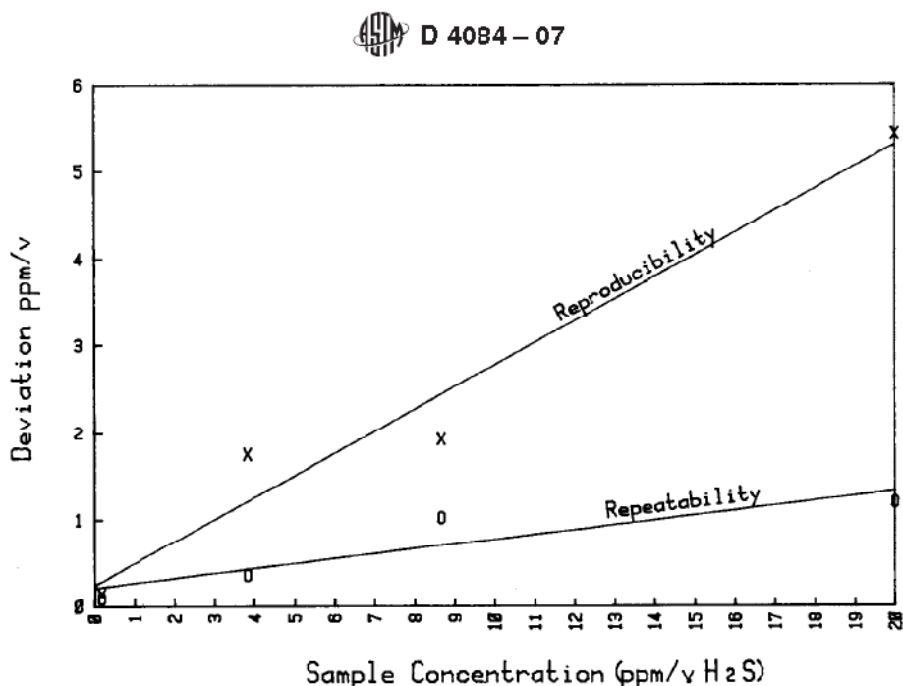
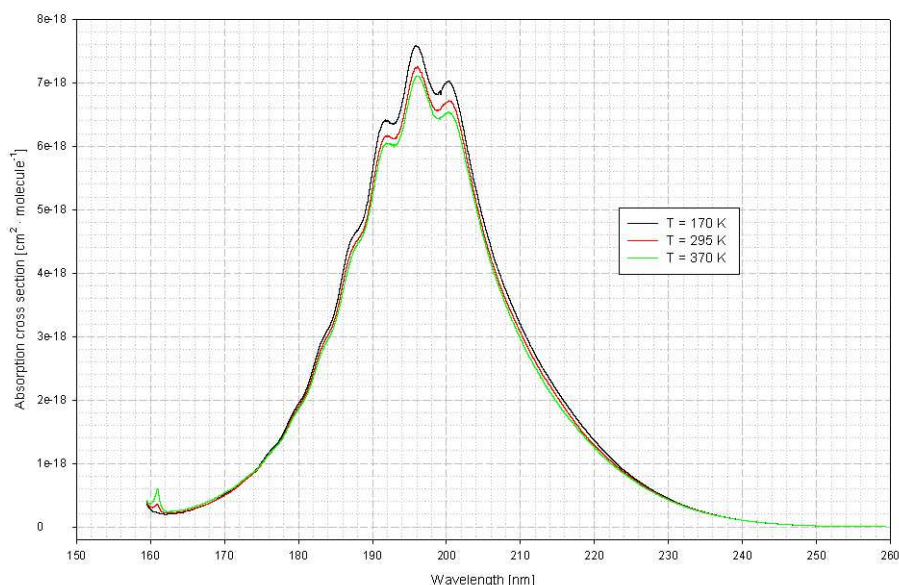


Figure 14: Graph of Reproducibility and Repeatability of the ASTM D4084-07 (20)

The Repeatability and Reproducibility should be considered suspect if they differ by more than those indicated in Figure 14 (20).

2.3.8 UV Spectrometry

Ultra Violet (UV) Spectrometry (32) is a method for detecting low levels of H₂S in Hydrocarbon- and Flue gas. H₂S strongly absorbs UV light in the far UV and is measured at a wavelength of preferably 228nm to minimize interferences from other species (hydrocarbons). Using UV spectrometry different methods are possible, dispersive, where the optical bench consists of a continuous UV light source (e.g. a deuterium lamp) with a grating to select the proper wave length or non-dispersive where the source is either a discontinuous source (e.g. a Cadmium discharge lamp) which will radiate discrete spectral lines (Cadmium 228nm measure and 326nm reference wavelength) or a continuous source with one or more filters to select the proper wave length for absorption of the component. When interferences are present or low levels (0-5ppm/0-25ppm) H₂S are measured a special technique, called frontal elution, is applied. The frontal elution technique uses chromatographic columns to separate and back-flush the potential interferences present in for example natural gas from the sulphur components (H₂S, COS and CH₃SH). In another technique the H₂S is bubbled through a NH₃-Water (ammonium hydroxide) solution and mixed to form ammonium sulphide in water. This solution is then fed to the analyser for measurement. Since the ammonium sulphide has much stronger absorption in the liquid phase than H₂S in the gas phase, much lower (0-5ppm) quantities can be detected and interferences will not reach the detector.



Temperature dependence of the absorption spectrum of hydrogen sulfide H₂S,
Wu and Chen, J. Quant. Spectrosc. Radiat. Transfer 60 (1998) 17

Figure 15: UV Spectrum of H₂S

Interferences can be compensated by the use of multi wavelength technique. The UV spectrometer measures the interfering components at different wavelengths than the wavelength of the component of interest and compensates the measurement with the interfering data.

Due to the robust sample cell set-up the technique can operate at high temperatures (500°C) and pressures (350kPa-15MPa) and can be used to run at high levels of H₂S (0-100%) and SO₂ (0-10%) (specific sulphur recovery applications (33)).

Ranges and repeatability's for the different UV techniques are displayed in Table 10 (32)

Table 10: Ranges and repeatability's for H₂S and SO₂ based on UV technique

UV technique	Component	wave length	model (32)	Range	Repeatability
Cd lamp non-dispersive (nd)	H ₂ S	228nm	933	0-5ppm 0-25ppm	1%
Ammonium Sulphide method nd	H ₂ S	228nm	4660	0-5ppm 0-300ppm	1%
Ammonium Sulphide method dispersive	H ₂ S	228nm	IPS-4	0-10ppm	2%
Cd lamp non-dispersive filter wheel	H ₂ S	228nm	921	0-25ppm	1%
Mn/Ni lamp non-dispersive filter wheel	SO ₂	280nm	921	0-25ppm	1%
Cd lamp non-dispersive filter wheel	H ₂ S	228nm	922	0-50ppm	1%
Mn/Ni lamp non-dispersive filter wheel	SO ₂	280nm	922	0-100ppm	1%



2.3.9 Diode array spectroscopy

Diode array spectroscopy (18) uses a tungsten, xenon flash, or deuterium light source as the optical source, and uses the continuous spectrum over an wavelength of 190-800nm or 400-1100nm. The analyser uses fibre optics to transmit the light through the sample in the flow cell. The adsorption spectrum is generated by a holographic grating and a diode array with 1024 detectors. It is a continuous spectrometer without moving parts. The resolution of the grating is reported as 1nm.

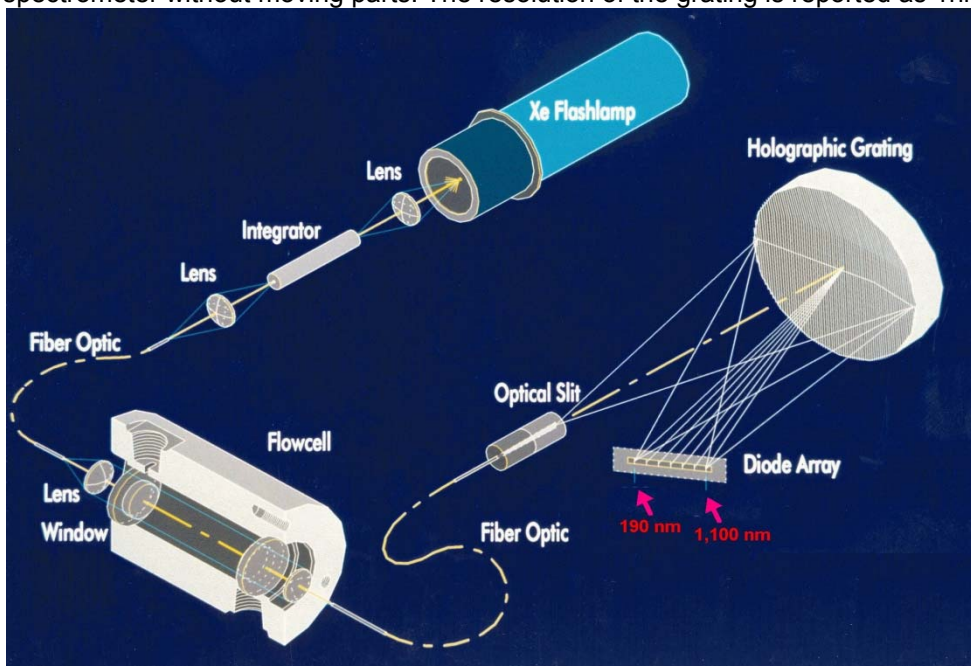


Figure 16: Diode array spectrophotometer (18)

The data for the sulphur applications using absorbance techniques is displayed in Table 11.

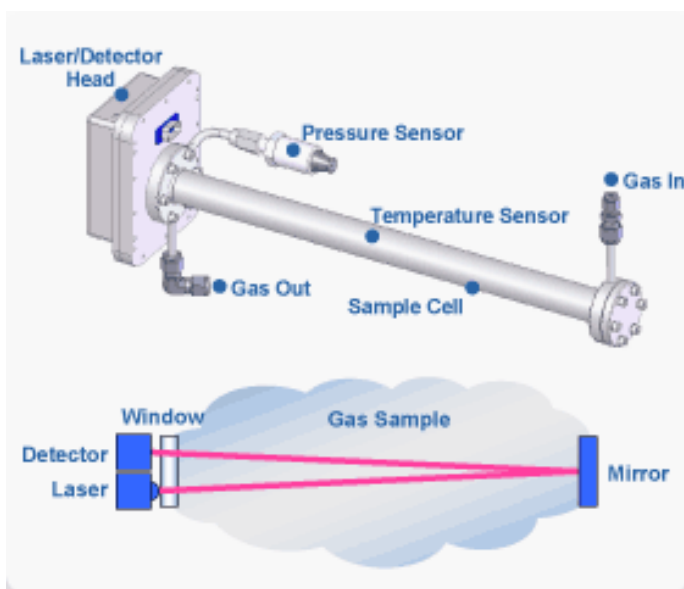
Table 11: Sulphur applications using UV absorbance techniques (18)

Site	Application	Phase	Repeatability
H ₂ S in 'sweet gas'	H ₂ S 0-10PPM	Gas	1%
Pre SRU	H ₂ S 0-100%	Gas	1%
Tail gas	H ₂ S 0-2%, SO ₂ 0-1%	Gas	1%
H ₂ S in natural gas	H ₂ S PPM RSH %	Gas	1%
SO ₂ and ammonia in stack	SO ₂ 0-500 PPM	Gas	1%
Sulphur in oil	Total Sulphur 0-10 PPM	Liquid (head space to be measured)	1%
H ₂ S in water	0-10 PPM	Liquid	1%

The fibre optics allows the sample cell to be installed away from the source, electronics and detector or the use of a direct sample probe. Due to the use of a holographic grating in combination with 1024 diode array detector the instrument is capable of analysing multi component species without the use of moving parts. It suffers though from the same interferences as described with the UV technique and has less linearity compared to spectrometers which uses discrete spectral line light sources.

2.3.10 Tunable Diode Laser Absorption Spectroscopy (TDLAS)

Tunable Diode Laser Absorption Spectroscopy (TDLAS) (11) uses a tunable near infrared Laser. A Tuneable Diode Laser is a type of semiconductor based laser that can be tuned to optically select a very specific wavelength (or colour) of light. The laser emits near-infrared radiation (1.2 - 2.5 μm , or 4000 - 8500 cm^{-1}) with a line width less than 0.003 cm^{-1} , which is narrower than molecular absorption line widths (typically 0.1 cm^{-1} at atmospheric pressure). Tuning to a specific wavelength is done by varying the diode temperature and the diode current going through it.



As the light passes through the gas sample, energy is absorbed, reducing the amount of light arriving at the detector. The length of the laser beam affects the sensor's sensitivity; hence a dual-pass optical path in most applications required (some applications require a number of passes).

Figure 17: Illustrative representations of a TDLAS Analyser and Sample Cell (34)

The minimum range for H_2S is 20ppm with a 500ppb sensitivity and it requires a multi path "Herriot" cell (34).

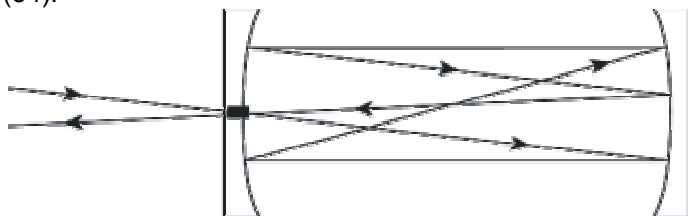


Figure 18: The Herriot cell features two spherical mirrors separated by slightly less than their diameter of curvature. Light enters through a hole in one and completes a number of passes before it exits through the same hole (35).

Sulphur compounds are relatively weak absorbers in the near infrared. When the sample is extracted from a process line or stack the TDLAS system requires a 28 meter multi-pass "Herriott" cell to achieve a repeatability value of 500 ppb in the range of 0-20ppm H_2S . The "Herriott" cell pressures is limited to an operating level of 10 psig (11).

The instrument allows an installation in a stack, pipeline or flare and is then able to measure over a relative large distance. As an example a TDL fence-line monitoring system has been in operation at the TOSCO refinery in Rodeo, California, since 1997. The system consists of two systems along the north and south fence lines of the plant. The one-way optical path of the north fence line is 930 m long and the south path is 955 m. Both systems are set to monitor every five minutes and to sound an alarm if concentration exceed a pre-set concentration level. The system is capable of generating a report with the system performance and the chemicals detected, their concentrations, and the system detection limits. The TDL system monitors for H₂S and NH₃. The concentration data in ppm are transferred to refinery computers (35).

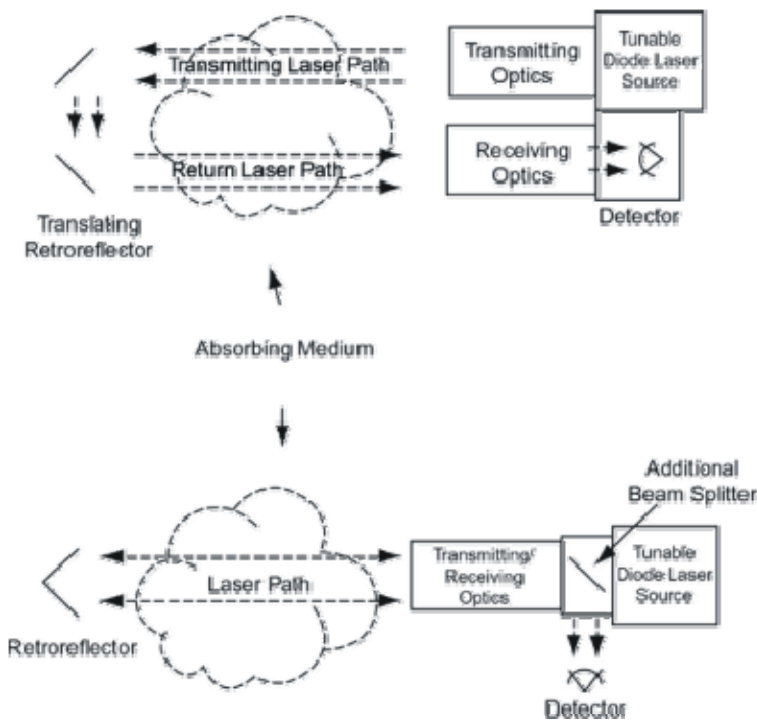


Figure 19: Open Air analytical set-up using Tunable Diode Laser (35)

The ranges, repeatability and LODs for Tunable Diode Laser on a H₂S applications in natural gas, flare gas and fuel gas are displayed in Table 12 (34).

Table 12: Ranges, repeatability and LODs for Tunable Diode Laser on H₂S applications (34)

TDL Application	Range	Repeatability	LDQ
H ₂ S in Natural gas	0-20ppm	5%	500ppb
H ₂ S in Flare gas	0-10ppm 0-300ppm	+/-0.5ppm 2%	500ppb
H ₂ S in Fuel gas	0-10ppm 0-300ppm	+/-0.5ppm 2%	500ppb

Literature (36) about the TDLAS states that UV spectroscopy suffers from misreading due to interfering components in the background gas and Gas Chromatography is to be highly complex, next to a high cost of service and consumables in respect to a TDLAS.

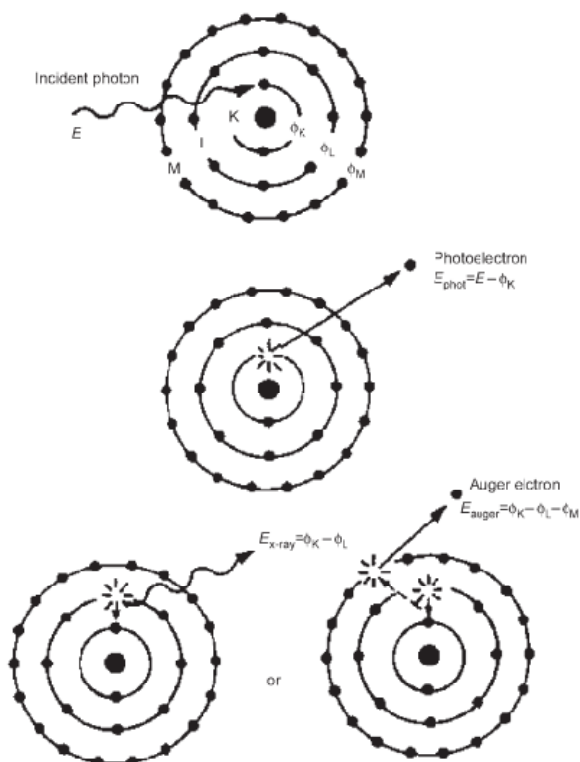
2.3.11 X-Ray spectroscopy

X-Ray spectroscopy (20) for determination of elemental sulphur in liquid products in the 0.025nm – 1nm spectrum (röntgen). The D2622 method describes a sulphur absorption at 0.5373nm and a reference at 0.5190nm or 0.5437nm. The method dictates a Wavelength Dispersive X-Ray Fluorescence Spectrometer (WDXRF), equipped for X-ray detection in the wavelength range from 0.52 – 0.55nm. The analysing crystal must be suitable for the dispersion of sulphur K α and background X-rays. The X-ray tube, should be capable of exciting sulphur K α radiation, anode types of rhodium, chromium, and scandium are most used. The detector, for detecting the X-rays, should be capable of measuring in the wavelength range of interest (0.52 – 0.55nm).

Interferences that are to be expected in fuels may not exceed the values as displayed in Table 13:

Table 13: Concentrations of interfering species

Species	Mass %
Phosphorus	0.3
Zinc	0.6
Barium	0.8
Lead	0.9
Calcium	1
Chlorine	3
Oxygen	2.8
FAME	25
Ethanol	8.6
Methanol	6



The photoelectric effect; X-ray fluorescence: In the photoelectric absorption process (see Figure 20), a photon is completely absorbed by the atom and an (inner shell) electron is ejected. Part of the photon is used to overcome the binding energy ϕ of the electron and the rest is transferred to the electron in the form of kinetic energy. After the interaction, the atom (actually an ion now) is left in a highly excited state since a vacancy has been created in one of the inner shells. The atom will almost immediately return to a more stable electron configuration by emitting an Auger electron or a characteristic X-ray photon. The latter process is called XRF (37).

Figure 20: Photoelectric ionization can be followed by either radiative relaxation, causing the emission of characteristic fluorescent X-rays or non-radiative relaxation, involving the emission of Auger electrons. (37)

The repeatability and reproducibility values for sulphur in all sample types as reported by the D2622 (20) are displayed in Table 14:

Table 14: Repeatability and reproducibility values for sulphur in Fuels

S,mg/kg	Repeatability mg/kg	Reproducibility mg/kg	Repeatability %	Reproducibility %
3.0	0.4	1.0	13%	33%
5.0	0.5	1.6	10%	32%
10.0	0.9	2.7	9%	27%
25.0	1.9	5.6	8%	22%
50.0	3.4	9.8	7%	20%
100.0	5.9	17.1	6%	17%
500	21	62	4%	12%
1000	37	108	4%	11%
5000	135	394	3%	8%
10000	235	687	2%	7%
46000	798	2333	2%	5%

2.3.12 Cavity Ring-Down Spectroscopy (CRDS)

Cavity Ring-Down Spectroscopy (CRDS) did not report any reference material in the literature on sulphur containing components in fuel or flue gasses. Due to the principle of measurement of a laser with CRDS is a technique which has the ability to detect H₂S at ppb levels (19).

2.3.13 Photo-ionisation, Titrimetric, and Conductimetric

The techniques using Photo-ionisation, Titrimetric, and Conductimetric (17) are limited in use and therefore not further discussed during this literature study.

3 Personal critical opinion

Regulation for the control of emissions state a gradual decreasing limit of emission. Analysers measuring and controlling the amount of pollutant emitted must be able to measure at such low levels.

The restriction and consequent techniques to recover sulphur species is mainly a health protection issue and in 2nd place a corrosive problem of buildings, monuments and industrial installations.

Sulphur is less present in the higher atmospheric layers due to the relative short residence time (4-7 days) in the troposphere (the 1st 20km of the atmosphere). Therefore it cannot easily penetrate to the stratosphere where greenhouse gasses have their largest negative effect. Sulphur will precipitate back to earth in the form of acid rain and it will have strong negative effects on the human health during smog conditions and it has corrosive effects on buildings, monuments and industrial installations.

The emission of sulphur can directly be related to diseases and deaths (3) and it is therefore strongly recommended to reduce the amount of sulphur emissions much further than that dictated today. New industrial countries are often reluctant to join the emission reduction programs (e.g. the Kyoto-protocol) but the contradiction in this is that the economic growth is initiated to enhance the human live conditions which can only be reached when extra emissions are avoided.

Gas Chromatographic methods for determination of (low) sulphur containing components is versatility and can be achieved using different detectors resulting in a wide dynamic range. (AED and SCD best for laboratory method of low sulphur containing component determination, FPD and PFPD best for laboratory and industrial (ASTM) method low sulphur containing component determination. μ TCD in combination with μ DMD would be good industrial method to cover low and high levels of sulphur containing components but no ASTM method is available yet for this application. Total sulphur methods are available using the sum of the individual components or total oxidation of sulphur to SO_2 . the summation method will allow reporting of individual components and provide information about specific (harmful) components. GC methods in general do not suffer from interferences as with optical methods due to the use of chromatographic separation columns. A wide variety of these columns are available. Disadvantages are the utilities necessary as the carrier, drift gas and cycle times. μ Gc overcomes this problem as it uses fast columns, which results in much shorter cycle times (30-60sec).

Sulphur containing components have the tendency to adsorb to the sample lines. Therefore the materials used for the sample wetted part are critical for the success of the determination of low sulphur containing components. Calibration and validation of the sulphur analyses are recommended on a calibration standard at ppm level with a dilution system or using a permeation system set-up. Low (ppb) levels of sulphur in a calibration standard using bottles is not recommended for the same adsorption problems. Low dead volume sample handling is required to minimize cross interference between analysis cycles.

Literature (12) describes the unrealistic use of a TCD detector for low determination of sulphur components. The μ TCD with the use of μ GC technology in combination with capillary columns will allow for low ppm level determination of sulphur components in different backgrounds. The μ GC in combination with standard GC technology is available and can be used to detect the sulphur containing components in different backgrounds.

ASTM Norms are a good way to test the equipment according a reference but the norm may be out dated as newer techniques become gradually available (38). Therefore a critical choice must be made whether to chose old referenced techniques or newer not tested/proven technology.

Lead acetate sulphur analyses has a number of ASTM approvals and is therefore widely used for H_2S and total sulphur determination, the technique is relatively strong influenced by temperature, sample pressure fluctuations and tape breakage. The initial costs of a lead acetate sulphur analyser are relative low but the operational costs are relative high. The lead acetate tape is a relative expensive and toxic



consumable, leakage in the tape cartridge leads to damage of the entire tape. Cycle times of 3 minutes and repeatability of 10% RSD is relative poor compared to other techniques (optical and μGC). It is therefore an outdated technique candidate for replacement by more modern techniques as UV spectroscopy, XRF, Laser and (fast) chromatography.

UV technique for sulphur measurement is a continuous and fast optical technique for determination of sulphur containing components. Low levels (0-5ppm) of H_2S and SO_2 can be measured in the different matrixes. The technique suffers from interferences from hydrocarbons but different compensating features are available to account for the interferences. The sample which is fed to a optical sample cell can be maintained at high pressure and temperature if necessary, which, will exclude complex sample handling steps as with other techniques (i.e. paper tape, GC). Single beam photometers with a beam splitter have the advantage of no moving parts which makes the instrument very robust in comparison with filter wheel techniques or instruments with a moving grating. Light sources with discrete spectral lines suffer less from spectral shift and linearity problems compared to continuous light sources with filter wheels or gratings.

Diode array spectroscopy is a optical technique as with the described UV technique for the continuous and fast determination of sulphur containing components. Low levels of H_2S (0-10ppm) and SO_2 (0-500ppm) can be measured in the different matrixes. The fibre optics allows the sample cell to be installed away from the source, electronics and detector or the use of a direct sample probe. Due to the use of a holographic grating in combination with 1024 diode array detector the instrument is capable of analysing multi component species without the use of moving parts. It suffers though from the same interferences as described with the UV technique and has less linearity compared to spectrometers which uses discrete spectral line light sources.

Tunable Diode Laser Absorption Spectroscopy (TDLAS) is a fast analytical technique that can be used for single component (H_2S) measurement in moderate ranges (0-20ppm). An advantage is the ability to place the analytical device direct on a stack or use an open path track in a plant to monitor H_2S in ambient air. Direct pipeline installation will avoid the release of analyser sample waste gas. The sample will not be in direct contact with the source and detector, which will minimize contamination of the analytical device. To reach the intended detection limits the device requires a multi pass sample cell system. Literature (36) about the TDLAS states that UV spectroscopy suffers from misreading due to interfering components in the background gas and Gas Chromatography is to be highly complex, next to a high cost of service and consumables in respect to a TDLAS. Current UV techniques (11) uses high reliable compensation techniques for interfering components eliminating misreading. As stated in (39) new micro-GC developments allow for low detection of H_2S using a micro-TCD. TDLAS is sensitive to spectral shifting due to temperature fluctuations, a way to overcome this problem is the use of a reference cell filled with the measured component as mentioned by (40) for the measurement of moisture in natural gas. An automatic routine will correct for the spectral shifting of the peak by locking the laser to the components absorption line (40). This reference cell can also be used for verification of component concentration.

X-Ray Fluorescence spectroscopy (XRF) is one of the few techniques for the determination of total sulphur in liquid fuels (e.g. naphtha, gasoline, diesel), other techniques (28) using the gas chromatographic method in conjunction with a pyrolyzer to convert the sulphur species to SO_2 are only feasible for total sulphur in relative light liquid fuels (e.g. naphtha and gasoline). In the lower ranges (0-5ppm, 0-10ppm) the gas chromatographic method is more precise (RSD=3%) than the XRF method (RSD=10%) and this is the range that is of most interest for environmental issues. XRF is faster (200-600sec) than GC (720sec).

Cavity Ring-Down Spectroscopy (CRDS) did not report any reference material in the literature on sulphur containing components in fuel or flue gasses. Due to the principle of measurement of a laser with CRDS is a technique which has the ability to detect H_2S at ppb levels (19).

The techniques using Photo-ionisation, Titrimetric, and Conductimetric (17) are limited in use and therefore not further discussed during this literature study.

4 Conclusions

A wide variety of analytical techniques are available for the determination of sulphur components in Flue gas, Fuel gas and Natural gas in different ranges. The literature research focuses on the determination of H₂S in Natural gas (0-5/120ppm), Fuel gas (0-2500ppm) and Flue gas (0-5/10ppm), the determination of SO₂ in Flue gas (0-1ppm) and the determination of Total Sulphur in Natural gas (0-5ppm) and Liquid fuels (0-10ppm) (e.g. Naphtha, Diesel).

The measurement of sulphur components is important for health, environmental and industrial (corrosion) protection.

Environmental regulation require a gradually further decreasing emission of pollutants. The analytical techniques that are developed and enhanced over time are gradually able to detect these pollutants at the required (lower) quantities.

New techniques developed for the mentioned measurements are; Laser spectroscopy for the measurement of H₂S at moderate ranges (0-20ppm) are feasible with Tuneable Diode Laser Absorption Spectroscopy (TDLAS). Low levels of H₂S (0-10ppm) and SO₂ (0-500ppm) are feasible with Diode array spectroscopy. TDLAS suffers from spectral shifting which can be compensated for using a new peak locking technique using a reference cell filled with the measured component. The reference cell can also be used for verification purposes. Both techniques are fast (30-60sec) and have the advantage to have no sample contact and direct in-line measurement. The Micro-Gas Chromatography with micro-Thermal Conductivity and Different Mobility Detection (DMD) can be used for the fast (30-60sec) measurement of H₂S and SO₂ (0.01-2500ppm) and can be extended with the measurement of other sulphur species. The micro-GC requires (small) amounts of Helium carrier gas and when the DMD is used Air is needed as a transport gas. In the range of 0.5-5ppm H₂S the μ TCD is sufficient for the analyses. Other Chromatographic detectors (FPD/PFPD/SCD and AED) allow for low determination (5-50ppb LODs) of (total) sulphur components and a combination with a pyrolizer and FPD can be used for low determination (0-5ppm) in liquid fuels (naphtha and diesel).

Existing and proven techniques are UV spectroscopy, Lead acetate and X-Ray Fluorescence spectroscopy. Lead acetate suffers from temperature and pressure fluctuations and has therefore a moderate repeatability (10%) is a relative slow technique (180sec) with a high consumable toxic waste. The measurement is in the range of 0.01ppm to percentage level (H₂S and Total Sulphur in gases) and has a number of ASTM approvals. The unit is therefore widely in use. UV spectroscopy is robust technique as the analyser has minimum sample contact, the sample cell can be operated at high temperatures (500°C) and pressures (350kPa-15MPa). The technique suffers from interference from matrix components but has advanced algorithms/techniques for interference compensation/prevention (multi wavelength/frontal elution). The technique is fast (<30sec) and can operate in a minimum range of 0.1-5ppm up to high percentage levels H₂S and SO₂ and has lower detection limits in comparison to TDLAS. X-Ray Fluorescence spectroscopy is one of the few techniques for the direct determination of total sulphur in liquid fuels (e.g. naphtha, gasoline, diesel) in the range of 1ppm to percentage levels within 200-600 seconds. As compared to the gas chromatographic method, which uses a pyrolizer to convert the sulphur species to SO₂, are only feasible for total sulphur in relative light liquid fuels (e.g. naphtha and gasoline). In the lower ranges (0-5ppm, 0-10ppm) the gas chromatographic method is more precise (RSD=3%) than the XRF method (RSD=10%).

Overall can be concluded that best analytical technique for sulphur containing components based on their ranges, repeatability's and speed can be addressed as follows:

For total sulphur in liquids, XRF is the best technique for total sulphur in diesel and GC with FPD and pyrolyzer for low quantities in naphtha and gasoline. XRF is faster (200-600sec) than GC (720sec). For the gas phase matrixes TDLAS & UV technique are best for high and moderate levels (>20ppm) of H₂S and SO₂. For direct in stack or open path measurement TDLAS is best. UV and UV Diode array spectrometry are best for low H₂S (0-5/10ppm) and SO₂ (0-1ppm) determination. Both have the advantage of speed (<30sec) and minimum sample contact. GC and μ GC (DMD) are best for ultra low detection (5/200ppb), μ GC in combination with μ TCD is an interesting alternative for low determination of H₂S (0.5-5ppm) as well as higher (2500ppm) concentrations.



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Appendix 1: ASTM (American Standard Test Methods)

Note: all mentioned ppm concentrations in the literature thesis are volume based, unless otherwise stated.

6 Appendix

6.1 Appendix 1: ASTM (American Standard Test Methods) (20)

ASTM #	Title	Application
D 4045-99	Sulphur in petroleum products by hydrogenolysis and rateometric colourimetry.	Injection by syringe 20 ppb to 10 ppm by weight of sulphur in liquids into a lead acetate paper tape H ₂ S analyzer equipped with a hydrogen reaction furnace.
D 2420-96	Hydrogen sulphide in liquefied petroleum (LP) gases (lead acetate method).	Manual pass/fail test for ppm of sulphur using lead acetate paper tape.
D2622-08	Test Method for Sulphur in Petroleum Products by X-Ray Spectrometry, 1999 Annual Book of ASTM Standards, Vol. 05.03	Covers 3mg/kg - 4.6 wt.% total sulphur diesel fuel, jet fuel, kerosene, other distillate oil, naphtha, residual oil, lubricating base oil, hydraulic oil, crude oil, unleaded gasoline, gasohol and biodiesel
D 4323-97	Hydrogen sulphide in the atmosphere by rate of change of reflectance.	Covers 1 to 3000 ppb by volume of H ₂ S in air using a lead acetate H ₂ S analyzer.
D 4468-95	Total sulphur in gaseous fuels by hydrogenolysis and rateometric colourimetry.	Covers 1 ppb to 20 ppm by volume of sulphur in gaseous fuels using a lead acetate H ₂ S analyzer equipped with hydrogen reaction furnace.
D 4810-94	Hydrogen sulphide in natural gas using length-of-stain detector tubes.	Covers .5 ppm to 40 % H ₂ S in natural gas using lead acetate in glass tubes. (commonly referred to the Drager test)
D 4084-94	Analysis of hydrogen sulphide in gaseous fuels (lead acetate reaction rate method).	Covers 1ppm to 16ppm (up to 100 % using dilution methods) by volume of sulphur in gaseous fuels using a lead acetate H ₂ S analyzer.
D5453-93	Test Method for Determination of Total Sulphur in Light Hydrocarbons, Motor Fuels and Oils by Ultraviolet Fluorescence, 1998 Annual Book of ASTM Standards, Vol. 05.03	Covers the 1.0-8000 mg.kg total sulphur analyses in naphtha's, distillates, engine oil, ethanol, Fatty Acid Methyl Ester (FAME), and engine fuel such as gasoline, oxygen enriched gasoline (ethanol blends, E-85, M-85, RFG), diesel, biodiesel, diesel/biodiesel blends, and jet fuel
D 5504-98	Standard test method for determination of sulphur compounds in natural gas and gaseous fuels by gas chromatography and chemiluminescence.	Covers 0.07 ppm to 690 ppm of individual sulphur compounds in gaseous fuels including natural gas, using sulphur chemiluminescence.



D 5623-99 (1999)	Standard test method for sulphur compounds in light petroleum liquids by gas chromatography and sulphur selective detection.	Covers 0.07 to 690 ppm of individual sulphur compounds in light petroleum gases using sulphur chemiluminescence.
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