Determination of total Sulfur and Nitrogen in Ambient Pressure Gases using the Gas Box Sampler, Accura and ElemeNtS

- Automated Introduction of Ambient Pressure Gases
- Rapid and Accurate Determination of Total Sulfur and Nitrogen
- Safety as a Priority with the Pressure Relief Valve
- Repeatability and Precision meeting ASTM requirements

Keywords: Sulfur, Nitrogen, Gases, D6667, Gas bags, Accura, UVF, CLD, ElemeNtS

Introduction:

Sulfur and nitrogen are natural components of hydrocarbon gases, unless it is removed during the production process. Both elements contribute to air pollution, so lowering their content contributes to the control of emissions. The sulfur content is often directly regulated in fuel specifications, while the nitrogen content is indirectly regulated with its effect on gum content and stability.

The preferred technique for sulfur determination in gases is combustion UV-fluorescence (UVF). An established test method using this technique is ASTM D6667. This test method is applicable to the analysis of natural, processed and final product gases containing sulfur in the range of 1 to 100 mg/kg. Nitrogen determination can be performed using the combustion chemiluminescence (CLD) technique. There is no established test method for nitrogen determination in gases. But the chemiluminescence technique can be used for it.

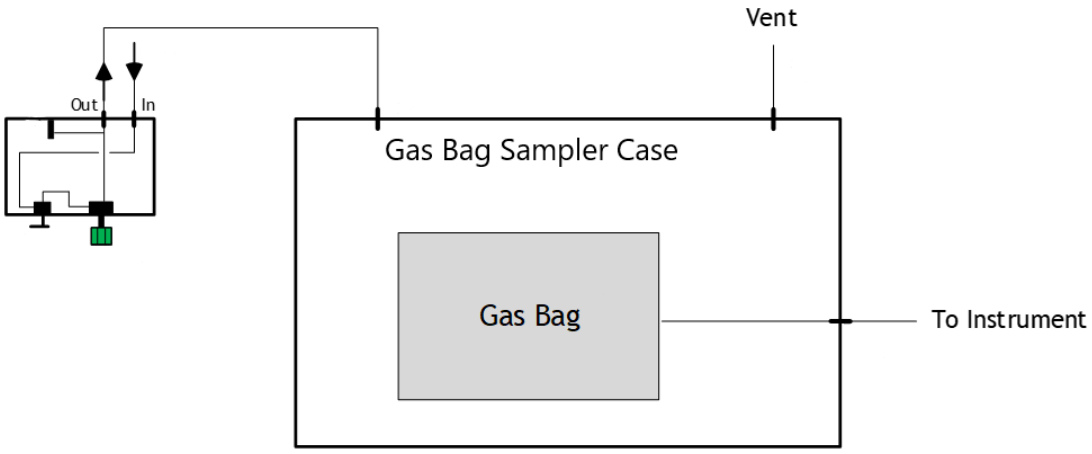
Gaseous streams in refineries and other chemical plants are often under high pressure. Taking a sample of such a stream requires the use of cylinders capable of withstanding these pressures. Cylinders under high pressure pose a certain hazard and safety precautions must be taken to prevent accidents. However, some streams have a low pressure, or a decision is made to lower the sample pressure at the time the sample is taken, and the sample is delivered to the laboratory in a Tedlar® bag at or slightly above atmospheric pressure.

Gas Box Sampler

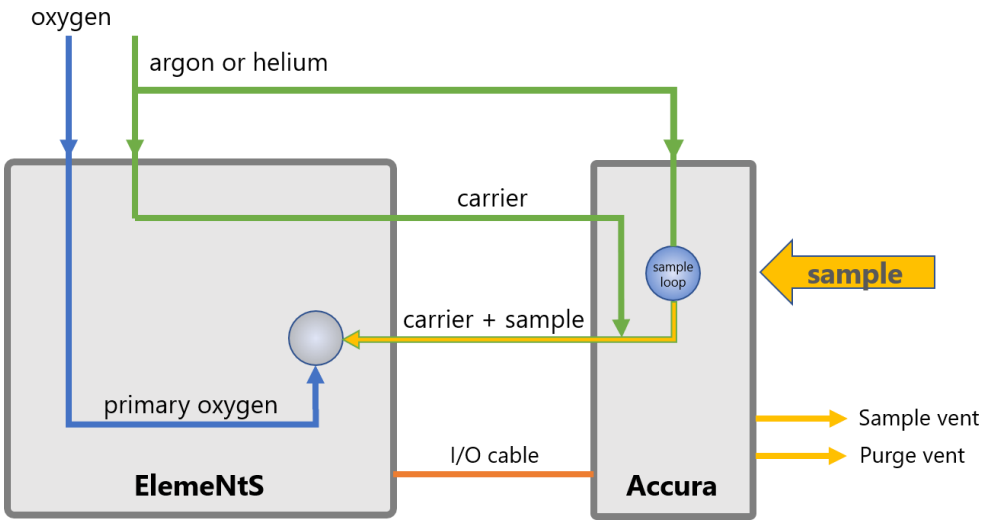
PAC offers a solution for the automated and safe introduction of ambient pressure gases into the ElemeNtS. The Gas Box Sampler (GBS) uses pressurized air or nitrogen to push the sample gas contained in a Tedlar® bag into the Accura, after which it is introduced into the Antek ElemeNtS for the analysis of its total sulfur and nitrogen content. By using pressurized air or nitrogen, the introduction is more automated than pressurizing the bag by other means, and operator time can be reduced.

The working principle of the GBS is based on the principle of applying pressure on the bag and thereby transferring the sample to the system. A (filled) gas bag is placed inside a semi-leak tight box, where it is connected to the sample line going to the Accura. The box is closed and a small overpressure (±0.2 bar) is created by means of a gas controlled by the gas supply box. This overpressure compresses the gas bag, causing the gas inside to flow towards the Accura. The vent on the case has a restriction, which will prevent the pressure from dropping too fast.

To prevent unsafe situations, the Gas Box Sampler is equipped with a pressure relief valve, which is adjusted to a pressure well below the limits of the box. In addition, the box is not completely leak tight, an increasing pressure will cause some leakage on the sealing on the lid of the box.



Using the vaporizer control valve on the Accura, the flow is regulated to 40-60 mL/min, ensuring that the 10 mL sample loop is completely flushed before each injection. After sufficient flushing, the 6-port valve is switched, and the content of the loop transferred to the ElemeNtS using an additional carrier gas stream.



Measuring principle

The sample coming from the Accura is introduced into a high temperature, dual zone combustion tube where the sample is vaporized and combusted. The released sulfur is oxidized to sulfur dioxide (SO_2) in an oxygen rich atmosphere. Nitrogen is oxidized to nitric oxide (NO).

$$R - S + R - N + O_2 \xrightarrow{1050°C} CO_2 + SO_2 + NO + H_2O + R$$

A stream of inert gas (helium or argon) transports the reaction products to the sulfur reaction chamber. In doing so, the gas passes through a membrane dryer that will remove the water vapor generated during combustion. In the sulfur reaction chamber the SO_2 molecules are excited by the absorption of energy of a UV source and emitting light (fluorescence) as it relaxes to a stable state.

$$SO_2 + hv \rightarrow SO_2^*$$
$$SO_2^* \rightarrow SO_2 + hv$$

A photomultiplier tube measures the emitted light and converts it into an electrical signal.

From the sulfur reaction chamber, the products are transferred to the nitrogen reaction chamber. This reaction chamber is kept under reduced pressure, using a build-in vacuum pump. Ozone is added to this reaction chamber, which reacts with the nitric oxide to form excited nitrogen dioxide (NO_2^*). Upon relaxing to the ground state, light is emitted (chemiluminescence).

$$NO + O_3 \rightarrow NO_2^* + O_2$$
$$NO_2^* \rightarrow NO_2 + hv$$

Again, a photomultiplier tube measures the emitted light and converts it into an electrical signal.

The response signal from both photomultiplier tubes is recorded over time and integrated to calculate the area. The sulfur and nitrogen concentrations of an unknown product is calculated using the linear regression function of the concentration of standard mixtures versus integrated area.

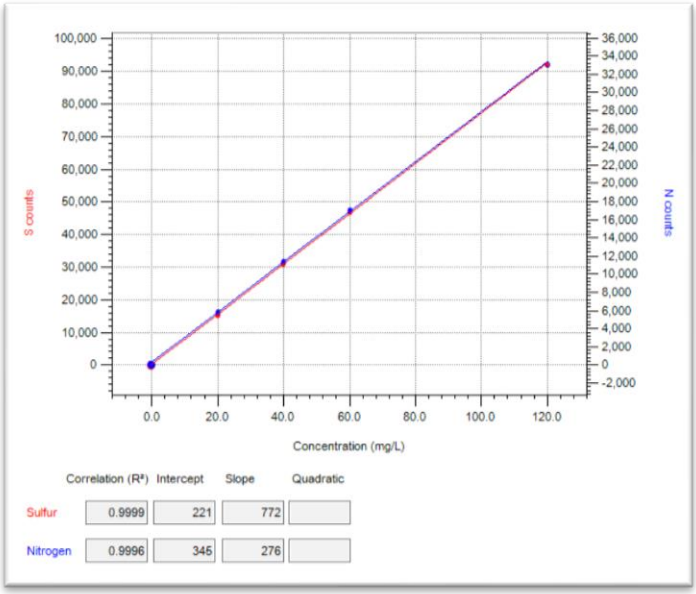
Validation

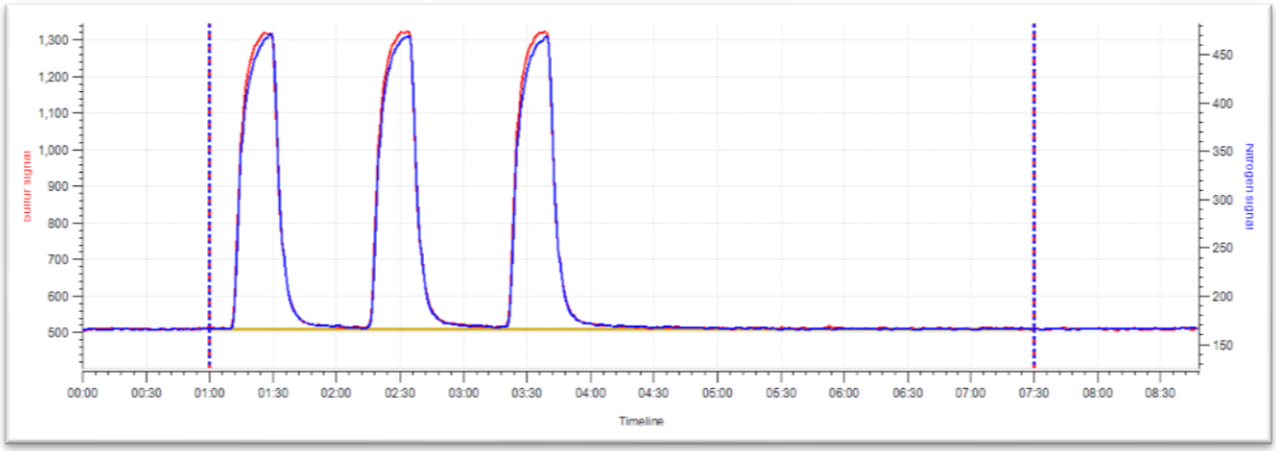
The Gas box sampler, Accura and Antek ElemeNtS total sulfur and nitrogen analyzer system and methodology are rigorously tested for response linearity, precision and accuracy, to validate its performance according to ASTM D6667 for sulfur and D4629 (indicatively) for nitrogen.

Calibration

A calibration curve is made using a single dimethyl sulfide and acetonitrile in iso-butane standard. Using the multiloop feature, multiple levels are injected. Each level and blank are measured three times. The ElemeNtS is linear in the complete range required by ASTM D6667 (0-100 mg/kg for gases).

Multiloop calibration 0-120 ppm mol		
Concentration ppm mol	**S counts**	**N counts**
0	-154	50
20	15662	5904
40	31237	11549
60	47178	17170
120	92574	33226
Slope	772	276
Intercept	222	345
Correlation	0.9999	0.9996





Recovery and precision

To determine the recovery and precision of the ElemeNtS, two gases, with different concentrations of sulfur or nitrogen, are transferred to two gas bags and analyzed using the gas box sampler and Accura. The obtained area counts are quantified using the multiloop calibration curve.

Gas X20A	
Component	**ppm mol**
Methyl mercaptan	10.18
Ethyl mercaptan	10.38
Carbonyl sulfide	10.18
Dimethyl sulfide	10.35
Hydrogen sulfide	10.18
Theoretical concentration	51.3
Analysis result	49.2
Δ Conc.	2.0
R D6667	16.1

Gas X20A contains 5 different sulfur components of around 10 ppm each, coming to a total of around 50 ppm. Using the ElemeNtS, a concentration of 49.2 ppm was found. The deviation from the theoretical concentration is well within the reproducibility of ASTM D6667, demonstrating the excellent precision of the ElemeNtS combined with the gas box sampler and Accura.

Gas X10A				
Sulfur			**Nitrogen**	
Component	**ppm mol**		**Component**	**ppm mol**
SO2	10.0		NOx*	10.15*
			NO	10.15
Theoretical concentration	10.0		Theoretical concentration	20.3*
Analysis result	9.7		Analysis result	14.6
Δ Conc.	0.3		Δ Conc.	5.7
R_{D6667}	3.1		R_{D4629}	3.8
			* not completely quantifiable	

Gas X10A contains sulfur dioxide and nitric oxide as well as higher nitrogen oxides, coming to a total concentration of 10 ppm for sulfur and around 20 ppm for nitrogen. Using the ElemeNtS, 9.7 ppm of sulfur was found. Again, this is well within the reproducibility of ASTM D6667.

The NOx in the X10A gas is not quantifiable in the same way as NO using the chemiluminescence technique, no conclusion can be made from this result. Consequently, the obtained concentration deviates from the theoretical concentration by more than the reproducibility of ASTM D4629. Like stated before, this ASTM method does not include gases or LPG's in its scope.

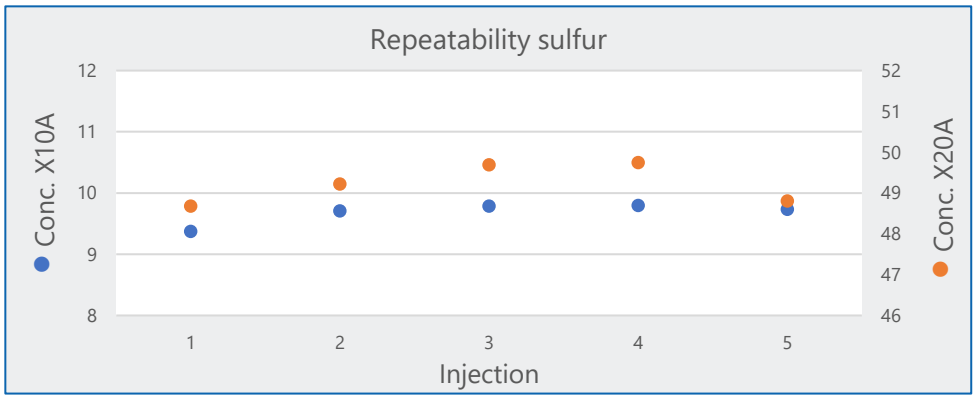
Repeatability

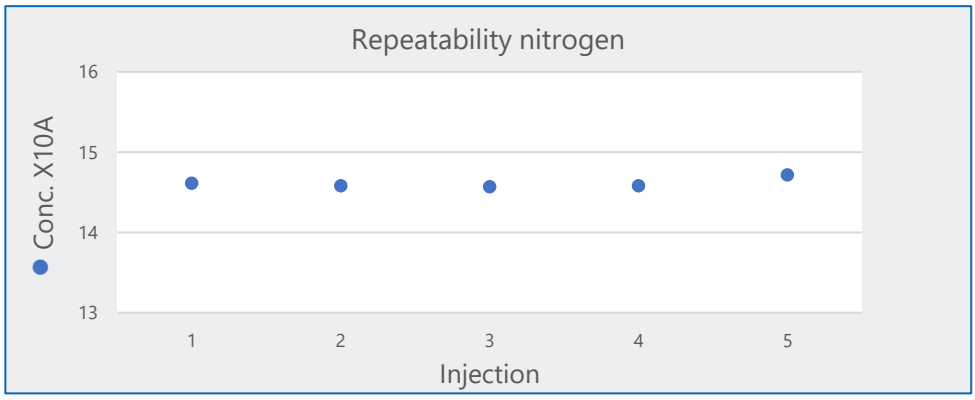
To validate the repeatability, the two gases contained in gas bags are measured 5 times consecutively. The repeatability is calculated and compared to the appropriate method (D6667 for sulfur and D4629 for nitrogen).

For both gases and both elements, the repeatability is well within the method requirements. Demonstrating the superb performance of the ElemeNtS analyzer combined with the gas box sampler and Accura.

Repeatability D6667 sulfur		
Injection	**X10A**	**X20A**
1	9.37	48.7
2	9.71	49.2
3	9.79	49.7
4	9.80	49.7
5	9.73	48.8
Average	9.68	49.2
Standard deviation	0.176	0.490
Repeatability (r)	0.49	1.36
Method Repeatability (r_{D6667})	1.11	5.67

Repeatability D4629 nitrogen	
Injection	**X10A**
1	14.6
2	14.6
3	14.6
4	14.6
5	14.7
Average	14.6
Standard deviation	0.060
Repeatability (r)	0.17
Method Repeatability (r_{D4629})	0.73





Conclusion

The gas box sampler combined with the Accura and ElemeNtS is an ideal tool to automate the analysis of total sulfur and nitrogen in ambient pressure gases. The results demonstrate that it meets and exceeds the requirements of both ASTM D6667 and D4629. Linearity is excellent, with a correlation coefficient of more than 0.999 over the concentration range of the method. Superb precision and repeatability exceed the requirements of both methods.

In addition to the analytical performance, the ElemeNtS has several other distinct advantages. Each analyzer is factory tested and comes with a start-up kit, allowing for fast commissioning. High degree of automation with the Accura and short analysis times of less than 5 minutes, enable large sample throughput. The 10" touchscreen can be used to fully control the instrument during daily use. Automated leak testing and the front maintenance door allow easy maintenance, making sure the analyzer maintains its superior performance. The safety features build into the ElemeNtS prevents hazardous situations and protects employees and assets from injuries and damage.

Please contact your local PAC representative for more information or a quote. We can provide both (online) demonstrations and the analysis of your samples, so you can observe the performance of the best sulfur and nitrogen analyzer on the market yourself.

Part number: AN-2020-E-017