Determination of Sulfuric Acid and Oleum Concentration

Relevant for: Chemical industry / Sulfuric acid production

Sulfuric acid is widely used in the chemical industry, plastics industry and petrochemistry, for the production of phosphoric acid as a starting material for fertilizers, in the metal industry (e.g. in etching baths), and in accumulators.

1. Quality control in sulfuric acid production

Sulfuric acid (H_2SO_4) is a high production volume chemical and plays an important role in various industries. Sulfuric acid is a colorless and odorless oily liquid which is highly hygroscopic. Depending on its concentration the acid is used for different purposes.

The production of sulfuric acid proceeds in several steps starting from sulfur dioxide SO_2. The biggest industry in need for sulfuric acid is the fertilizer production (approx. 50–60 % of the total H_2SO_4 production volume). The acid is also needed for the manufacturing of various goods and chemicals (e.g. hydrochloric and nitric acid, synthetic fibers, pigments). Other applications include the pickling process to remove impurities from metals, the recovery of metals and the application as electrolyte in storage batteries.

2. Concentration determination

2.1. General

Concentration determination for quality control and subsequently adjustment of process parameters is important in the production stage when concentrated sulfuric acid containing dissolved sulfur trioxide (SO_3) is diluted with water to the desired concentration.

Dissolving sulfur trioxide, SO_3, in concentrated sulfuric acid results in a fuming solution called oleum (or "fuming sulfuric acid"). Oleum is used in the chemical industry, for example for the production of intermediate materials or chemical fibers.

2.2. Conventional: Titration - a tedious method

The conventional method for determination of sulfuric acid concentration is titration. However, titration is not only time-consuming and hazardous, but also includes a range of error prone operation steps even for skilled laboratory staff.

The titration of sulfuric acid or oleum is carried out with a base, commonly sodium hydroxide, NaOH. The acid sample has to be diluted prior to titration - a time-consuming and hazardous operation. The accuracy of the results is influenced by several factors such as the skill of the operator, the quality of the standard base solution, the precision of the burettes, the quality of the indicator used, etc. In routine analysis accuracies of 0.1 % w/w to 0.5 % w/w H_2SO_4 can be attained.

2.3. The alternative: Density or density and sound velocity measurement

Anton Paar offers instruments for sulfuric acid as well as oleum measurements where concentration monitoring and quality control are needed.

Anton Paar instruments not only ensure safety for the operator but also high quality results: they are easy to use and operator independent. Neither sample preparation (e.g. dilution) nor additional chemicals are needed. A reliable density and/or sound velocity result is shown quickly and the conversion into concentration is performed automatically.

The density and sound velocity characteristics of sulfuric acid/oleum over the concentration range of 0 % to 114 % w/w H_2SO_4 and 0 to 65 % w/w free SO_3 (oleum) show that in some ranges the concentration

can be determined from the density result, and in other ranges from the sound velocity result. **Figure 1** graphically demonstrates that density measurement is absolutely sufficient in the concentration range from 0 % to 90 % H_2SO_4, but concentrations above 90 % need an additional parameter for clear concentration determination. Based on these findings, the measuring method "Sulfuric Acid & Oleum" was defined for DSA M, allowing the fast and accurate determination of sulfuric acid and oleum samples of any concentration.

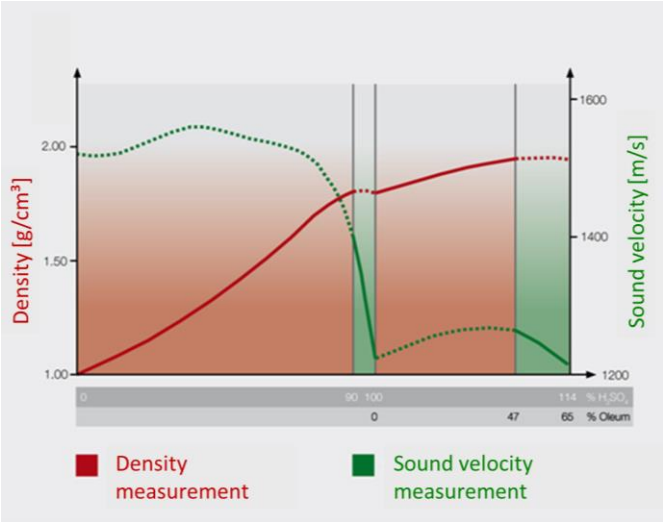

Figure 1: Density and sound velocity characteristics of sulfuric acid and oleum

Depending on required accuracy and acid concentration, several Anton Paar density meters offer themselves.

- DMA™ 35 & DMA™ 35 Ex portable density meters for quick density checks in the lab or for measurements directly from tanks or vessels in the field. DMA™ 35 Ex is intrinsically safe for the use in hazardous areas.
- DMA™ 501 and DMA™ 1001 stand-alone benchtop density meters for reliable analyses.
- DMA™ 4100/4500/5000 M laboratory instruments for quality control of raw, intermediate and final products.
- DSA 5000 M laboratory density and sound velocity meter for highly accurate concentration determination of sulfuric acid and oleum across the whole concentration range.

Table 5 summarizes the density meters suitable for the respective concentration ranges.

Table 5: Concentration range and required accuracy determine the suitability of the measuring instrument

Instrument	Sulfuric Acid [% w/w]	Accuracy [g/cm³]
DMA™ 35	0 - 90	±0.001 g/cm³
DMA™ 501	0 - 90	±0.001 g/cm³
DMA™ 1001	0 - 90	±0.0001 g/cm³
DMA™ 4100 M	0 - 90	±0.0001 g/cm³
DMA™ 4500 M	0 - 90	±0.00005 g/cm³
DMA™ 5000 M	0 - 90	±0.000007 g/cm³
DSA 5000 M	0 – 114 (0 % - 100 % sulfuric acid: 0 % - 65 % oleum)	±0.000007 g/cm³

3. Safe, fast, and reliable measurements

3.1. Filling sulfuric acid and oleum into DSA M

Only a small volume of approximately 3 mL sample is required, no sample preparation is needed. The sample is filled into the DSA 5000 M measuring cells by using a glass syringe or via an external peristaltic pump.

Tip: Inserting the glass tip of the syringe directly into the inlet adapter of DSA 5000 M may result in the fracture of the tip due to applied inappropriate pressure. Do not insert the syringe directly into a Teflon adapter, use a small piece of viton hose between the syringe and DSA 5000 M instead (see **Figure 2**).

Figure 2: Filling DSA 5000 M with a glass syringe

3.2. Titration versus DSA 5000 M results

3.2.1. General remarks

The following measurements were carried out to compare DSA 5000 M results with values obtained by titration (**Table 1** to **Table 4**). For this purpose different concentrations of H_2SO_4 and oleum were measured.

The measurement results show a very good agreement between titration and DSA 5000 M. Furthermore it should be marked that the standard deviation of titration results is constantly higher than of DSA 5000 M measurements.

3.2.2. 50 % w/w Sulfuric acid

Table 1: Comparison of titration and DSA 5000 M results, incl. mean value and standard deviation (s.d.); sample: 50 % w/w sulfuric acid

Number of measurement	Titration	DSA 5000 M
	Sulfuric Acid [% w/w]	*Sulfuric Acid [% w/w]*
1	47.92	47.88
2	47.95	47.88
3	47.81	47.88
mean value	**47.89**	**47.88**
s.d.	**0.07**	**0.00**

3.2.3. 96 % w/w Sulfuric acid

Table 2: Comparison of titration and DSA 5000 M results, incl. mean value and standard deviation (s.d.); sample: 96 % w/w sulfuric acid

Number of measurement	Titration	DSA 5000 M
	Sulfuric Acid [% w/w]	*Sulfuric Acid [% w/w]*
1	96.15	96.00
2	96.15	96.00
3	96.07	96.00
4	96.23	96.00
mean value	**96.15**	**96.00**
s.d.	**0.07**	**0.00**

3.2.4. 20 % w/w Oleum

Table 3: Comparison of titration and DSA 5000 M results, incl. mean value and standard deviation (s.d.); sample: 20 % w/w oleum

Number of measurement	Titration		DSA 5000 M	
	Sulfuric Acid [% w/w]	*Oleum [% w/w]*	*Sulfuric Acid [% w/w]*	*Oleum [% w/w]*
1	104.67	20.75	104.54	20.18
2	104.65	20.68	104.54	20.19
3	104.61	20.48	104.54	20.19
4	104.64	20.61	104.54	20.19
mean value	**104.64**	**20.62**	**104.54**	**20.19**
s.d.	**0.03**	**0.10**	**0.00**	**0.01**

3.2.5. 50 % w/w Oleum

Table 4: Comparison of titration and DSA 5000 M results, incl. mean value and standard deviation (s.d.); sample: 50 % w/w oleum

Number of measurement	Titration		DSA 5000 M	
	Sulfuric Acid [% w/w]	*Oleum [% w/w]*	*Sulfuric Acid [% w/w]*	*Oleum [% w/w]*
1	111.31	50.24	111.23	49.90
2	111.28	50.12	111.23	49.90
3	111.34	50.40	-	-
mean value	**111.31**	**50.26**	**111.23**	**49.90**
s.d.	**0.03**	**0.14**	**0.00**	**0.00**

4. Safety issues

4.1. Protective devices

Sulfuric acid and oleum cause very strong reactions: They destroy all kinds of tissue and fabric on contact. It is essential to observe all safety regulations regarding the handling, cleaning, rinsing of the samples and waste liquids. Avoid contact with the substance: Prevent skin/eye contact by using of impervious gloves, clothing, boots, apron, and eye goggles.

4.2. Dilution of sulfuric acid

Diluting with water must be performed with caution as this extremely exothermal reaction generates a large

amount of heat. The concentrated acid is always added to water and not the other way around.

4.3. Storage

Sulfuric acid should be safely stored in glass vessels or bottles.

4.4. Cleaning

Never flush out oleum or concentrated sulfuric acid with water. Always start the cleaning procedure with an acid which is weaker than the previously filled one. Follow the sequence, given in Figure 3, before cleaning with water.

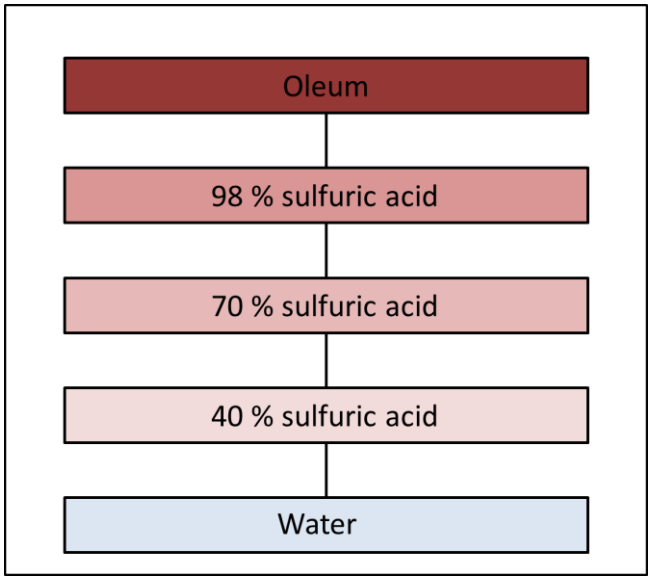

Figure 3: Cleaning liquid sequence for oleum and sulfuric acid

5. At a glance: Oleum analysis safe and accurate with DSA 5000 M

- DSA 5000 M provides measuring results unmatched in accuracy, independent of the operator, and enables to optimize product quality immediately.
- The automated measuring procedure is highly reliable, and avoids operating errors that are possible with e.g. titration.
- A measurement takes only 3 minutes. The conversion to concentration units is automatically carried out.
- The instrument can be connected to your Laboratory Information Management System (LIMS) using the Anton Paar software LIMS Bridge.
- The temperature is exactly controlled by an integrated Peltier thermostat.
- DSA 5000 M has a rugged construction, requires only small space in the lab and can also be operated on the production floor.

6. Process instruments from Anton Paar

Anton Paar also provides process measuring systems for the determination of sulfuric acid and oleum concentration. These density and sound velocity transducers work according to the same measurement principle as the DSA 5000 M bench-top analyzer.

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