

VGB PowerTech

Instruction Sheet

Analysis of FGD Gypsum

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P.O. Box 10 39 32, D-45039 Essen

Phone +49 0201 8128-200

Fax +49 0201 8128-329

E-mail: mark@vgb.org

<http://www.vgb.org>

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Preface

The first edition of the instruction sheet "Analysis of FGD gypsum" was elaborated and published by the joint Working Group of the

Bundesverbandes der Gipsindustrie e.V.

and

VGB PowerTech e.V.

to assure a high quality of FDG gypsum in coal-fired power plants. Due to new analysis methods the Project Group of the VGB Working Panel „Analysis“ revised the second edition and co-ordinated it with the Federal Association of the Gypsum Industry (Bundesverband der Gipsindustrie e.V.).

Essen, December 2008

VGB PowerTech e.V.

Introduction

Flue gas desulphurization (FGD) gypsum is understood as being the hydrated calcium sulphate ($\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$) produced within the flue gas desulphurization of power stations. In the following, FGD gypsum is also referred to as raw gypsum.

The analysis of FGD gypsum includes the chemical analysis of FGD gypsum constituents and the determination of further properties, which are defined in the quality requirements for gypsum as worked out by Bundesverband der Gipsindustrie as well as by Eurogypsum, VGB PowerTech and ECOBA.

It has to be pointed out that raw gypsum from different sampling points may lead to deviating analysis results. The sampling points as well as the extent of the analysis have to be co-ordinated between gypsum producers and customers.

The analytical methods described in Part I are applicable to reference analyses. Other methods can be used for continuous quality control purposes; they are described in Part II, Analytical Methods - Annex. Newer and/or more efficient methods can be used as well, provided equivalent results are achieved or the results only differ in a constant correlation factor. However, in this case a yield coordination between the laboratories of the power station (supplier) and the FGD gypsum processor (purchaser) is recommended.

The quality of the FGD gypsum should allow the production of products which are equivalent to those made of natural gypsum.

The actual quality requirements are defined in the common utilization concept of the gypsum processing and power production industries or in regulations to be agreed upon for each individual case.

Part III contains tables with chemical/physical data for the analysis of gypsum.

	Page
Part 1 Analytical methods	7
0 Preparation of samples and of stock solutions	7
0 Add. Production of FGD gypsum fired to stucco (Addition)	7
0.1 Acid decomposition	7
0.2 Aqueous extract	7
0.3 Alternative aqueous extract	8
0.4 Microwave decomposition for the determination of heavy metals	8
1 Determination of moisture, F	9
1.1 Gravimetric	9
1.2 Rapid dryer	9
1.3 Thermogravimetric	9
2 Determination of degree of purity R° (calcium sulphate dihydrate)	9
2.1 Gravimetric determination by crystallization water	9
2.2 Thermogravimetric determination by crystallization water	10
2.3 Gravimetric determination by sulphate	10
2.4 Complexometric determination by calcium	10
3 Thermogravimetric determination of moisture, degree of purity and calcium carbonate content (TGA)	11
4 Determination of the pH value	13
5 Determination of the degree of whiteness / colour of raw gypsum	14
6 Determination of the odour - perception	15
7 Determination of screening residues at 32 µm - air-jet screening	15
8 Minor constituents	15
8.1 Determination of magnesium by AAS as magnesium oxide	15
8.1.1 Magnesium (total)	16
8.1.2 Magnesium (water-soluble)	16
8.2 Determination of sodium by AAS as sodium oxide	17
8.2.1 Sodium (total)	18
8.2.2 Sodium (water-soluble)	18
8.3 Determination of potassium by AAS as potassium oxide	19
8.3.1 Potassium (total)	19
8.3.2 Potassium (water-soluble)	20
8.4 Determination of aluminium (total) by AAS as aluminium oxide	21

8.5	Determination of iron (total) by AAS as iron oxide	22
8.6	Determination of manganese (water-soluble) by AAS as manganese oxide	23
8.7	Determination of magnesium, sodium, potassium, aluminium, iron and manganese by inductive coupled plasma (ICP) OES as oxides	24
8.8	Determination of chloride	26
8.8.1	Potentiometric	26
8.8.2	Ionic-chromatographic	26
8.8.3	Titrimetric	28
8.9	Determination of sulphur dioxide (SO ₂) as calcium sulphite-hemihydrate - titrimetric with iodine	28
8.10	Determination of oxidable constituents as C, such as organic matter, soot, fly coke (C _{coke}) - selective determination with a carbon analyzer	29
8.11	Determination of „HCl-insolubles“ - gravimetric	30
8.12	Determination of carbonates as calcium carbonate	30
8.12.1	Acidimetric	30
8.12.2	Thermogravimetric	31
9	Determination of trace elements	31
Part 2 Annex to analysis methods		32
A 5	Determination of degree of whiteness / of colour of raw gypsum	33
A 7	Determination of particle size distribution by laser granulometry	33
A 8	Other constituents	34
A 8.8	Photometric determination of chloride	34
A 8.10	Technical examinations of gypsum binders	35
A 8.12	Determination of carbonates as calcium carbonate (indirect inorganic determination of carbon)	36
A 8.13	Determination of reactivity of limestone	37
Part 3 Chemical/physical tables for the determination of gypsum parameters		38
(I)	International atomic weights	39
(II)	Chemical formulas and molar masses of essential compounds related to gypsum	42
(III)	Conversion factors for flue gas desulphurization processes	43
(IV)	Characteristics of the phases in the system CaSO ₄ / H ₂ O	45

Part 1 Analytical methods

0 Preparation of samples and of stock solutions

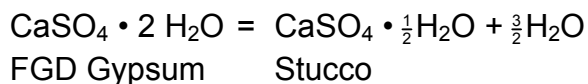
Some 200 g wet raw gypsum is required for the whole course of analysis. First a homogeneous sample is prepared by mixing and dividing the gypsum (following DIN 51701-1: 2007-12) until a sample weighing approx. 200 g is obtained. Thereof, 180 g are used for determining the moisture and, following this, for determining all the other properties. Where necessary. The remaining 20 g are stored in wet conditions for the determination of the pH value.

Note:

All sample preparation and moisture determination work shall be carried out steadily and without delay or interruption in order to avoid any loss of moisture. Where the samples are collected from gypsum deposits, they shall be transported in closed containers.

0 Add. Production of FGD gypsum fired to stucco (Addition)

1 kg \pm 0.001 kg dry raw gypsum is evenly spread out on a plate with a dumping height of max. 2 cm and is burned to stucco (calcium sulphate hemihydrate) in a drying chamber over 4 hours by 160 °C.



In accordance with the test specification of the DIN EN 13279-2: 2004-10 stucco can be used (see current number A 8.10) for technological examination.

0.1 Acid decomposition

Stock solution A1

Add some 30 ml hydrochloric acid, $\omega(\text{HCl}) = 16 \%$, (32 % HCl reagent-grade will be diluted with demineralized water proportionately 1 to 1) and some 120 ml demineralized water to approximately 1 g \pm 0.0005 g dry raw gypsum (E = initial weight in g) in a beaker. Then boil this mixture for 10 minutes. Afterwards filter it off through a membrane filter and wash the membrane filter with hot, demineralized water.

Put the filtrate into a 250 ml volumetric flask, and then fill the flask with demineralized water up to the mark. This stock solution A1 is used for the determination of the total content of magnesium, sodium, potassium aluminium and iron, calculated according to their oxides as described below.

0.2 Aqueous extract

Stock solution A2

Add some 50 g \pm 0.001 mg dry raw gypsum (E = initial weight in g) to approx. 400 ml hot, demineralized water in a 600 ml beaker. Then put the suspension on a heatable magnetic

stirrer and agitate for 10 minutes. Following this, pour the suspension into a 500 ml volumetric flask. When the suspension has cooled down fill the flask with water up to the mark and mix thoroughly. Finally, filter it through a membrane filter which was washed with hot, demineralized water before.

This stock solution A2 is used for determining the water-soluble constituents of magnesium, manganese, sodium and potassium - calculated as their appropriate oxides – as well as chloride as described below (see also note of current number 0.3).

Note:

For an accurate calculation, the volume of undissolved gypsum needs to be taken into consideration. At a density of 2.3 g/ml, approx. 49 g undissolved gypsum is equivalent to approx. 20 ml so that a volume of 480 ml should be used instead of 500 ml.

0.3 Alternative aqueous extract

Stock solution A3

Add some $1 \text{ g} \pm 0.0005 \text{ g}$ dry raw gypsum ($E =$ initial weight in g) to 180 ml demineralized water in a beaker and boil this solution for 10 minutes. Afterwards the solution is filtered through a membrane filter which was washed with hot, demineralized water before. In case of using a folded filter instead of a membrane filter the contamination of the filtrate by ingredients of the filter material is to be absolutely prevented due to the small initial weight of the sample.

The filtrate will be filled up in a 250 ml volumetric flask with demineralized water up to the mark. This alternative stock solution A3 is used for determining the water-soluble constituents of magnesium, manganese, sodium and potassium – calculated as their appropriate oxides – as well as chloride as described below.

Note:

In each case it has to be clarified with the gypsum customer, which stock solution has to be used regarding the water-soluble constituents – whether A2 (aqueous extract) or A3 (alternative aqueous extract).

0.4 Microwave decomposition for the determination of heavy metals

Stock solution A4

Add some $1 \text{ g} \pm 0.0005 \text{ g}$ dry raw gypsum to 10 ml nitric acid suprapur, $\omega(\text{HNO}_3) = 65 \%$, and 1 ml hydrofluoric acid suprapur, $\omega(\text{HF}) = 40 \%$, in the PTFE inset of a microwave decomposition equipment. Afterwards the mixture is heated up to $200 \text{ }^\circ\text{C}$ and thermally treated for 60 minutes. After cooling down 20 ml boric acid, $\omega(\text{H}_3\text{BO}_3) = 4 \%$, is added to the solution to complex the fluoride and is heated again for 1 hour at $140 - 160 \text{ }^\circ\text{C}$. After cooling the solution is given into a 100 ml silica volumetric flask and will be filled up to 100 ml with demineralized water and mixed. Then the solution will be filled up into a polyethylene bottle. A blank value solution without weighted sample is to be treated in the same way.

1 Determination of moisture

Alternatively to the drying chamber the thermogravimetric analysis (TGA) could be used.

1.1 Gravimetric

Procedure

Take approx. 180 g ± 0.01 g wet raw gypsum (E = initial weight in g) and dry in the drying chamber at 40 – 45 °C until its weight remains constant; then weigh it. A suitable vessel (low height) is to be used.

Calculation:

$$F (\%) = \frac{(E - A) \cdot 100}{E} \left(\frac{\text{g}}{\text{g}} \right)$$

1.2 Rapid dryer

Procedure:

30 – 35 g wet raw gypsum is weighed in the crucible of a rapid dryer. Between 40 – 50 °C the raw gypsum will be dried to a constant weight.

Calculation:

The indicated value of the rapid dryer system will be noted down. This value is equivalent to the moisture (H₂O) in %.

1.3 Thermogravimetric

See TGA-Method in No. 3.

2 Determination of degree of purity R° (calcium sulphate dihydrate)

2.1 Gravimetric determination by crystallization water

Procedure:

Weigh 3 – 5 g ± 0,0005 g dry raw gypsum (E = initial weight in g) into a crucible, dehydrate in a muffle furnace at 360 °C until the gypsum weight remains constant (30 - 60 min), then cool down in a desiccator and weigh without delay (A = final weight in g).

Calculation:

$$KW (\%) = \frac{(E - A) \cdot 100}{E} \left(\frac{\text{g}}{\text{g}} \right)$$

The degree of purity is derived from the content of crystallization water (KW). Pure calcium sulphate dihydrate contains 20.927175 % crystallization water.

$$R^{\circ} (\%) = \frac{KW \cdot 100}{20.927175} \left(\frac{\%}{1} \right)$$

2.2 Thermogravimetric determination by crystallization water

See TGA Method, current number 3.

2.3 Gravimetric determination by sulphate

Reagents:

- Barium chloride solution, ω (BaCl₂) = 10 %

Procedure:

The acid decomposition described in chapter 0.1 is used for the determination of the sulphate content.

Pipette 100 ml of stock solution A1, heat it to boil and add 25 ml of the barium chloride solution drop by drop while stirring; keep the mixture at the boil for several minutes. Leave the solution overnight, and then filter it using a filtering crucible of porosity 1 annealed at 900 °C and wash out the chloride with demineralized water. Ignite the residues in the crucible at 900 °C to constant weight, and weigh it (A = final weight in [g]: is equivalent to the weight difference of the crucible with and without barium sulphate, factor: SO₃/BaSO₄ = 0.34304528).

Calculation:

$$SO_3 (\%) = \frac{A \cdot 250 \cdot 0.34304528 \cdot 100}{E \cdot 100} \left(\frac{g \cdot ml}{ml \cdot g} \right)$$

E = initial weight (in g)

The degree of purity is calculated from the content of sulphur trioxide. Pure calcium sulphate dihydrate contains 46.5020971 % sulphur trioxide.

$$R^{\circ} (\%) = \frac{SO_3 \cdot 100}{46.5020971} \left(\frac{\%}{1} \right)$$

2.4 Complexometric determination by calcium

Reagents:

- disodiummethylenediaminetetraacetate (EDTA) solution, c (Na₂-EDTA) = 0.1 mol/l
- calconcarboxylic acid indicator
- triethanolamine
- sodium hydroxide solution, ω (NaOH) = 30 %

Procedure:

The acid decomposition described in chapter 0.1 is used for the complexometric determination of calcium oxide.

Pipette 50 ml of acid decomposition A1 into a 250 ml beaker (long tube) and add demineralized water to the 100 - 150 ml graduation. Add 10 ml triethanolamine to this

solution and adjust a pH value of 12 by adding sodium hydroxide solution. At this pH value, magnesium will precipitate as hydroxide. Thereafter, add a spatula-tipful of calconcarboxylic acid and titrate the EDTA solution using a micro burette and magnetic stirrer until the colour changes from wine red to blue. Though absorbing some of the indicator, the magnesium will not affect the colour change.

1 ml of the EDTA solution is equivalent to $4.0078 \cdot 10^{-3}$ g Ca (factor: CaO/Ca = 1.399207)

Calculation:

$$\text{Ca (\%)} = \frac{4.0078 \cdot 10^{-3} \cdot 250 \cdot V}{50 \cdot E} \cdot 1.399207 \cdot 100 \left(\frac{\text{g} \cdot \text{ml} \cdot \text{ml}}{\text{ml} \cdot \text{ml} \cdot \text{g}} \right)$$

V = EDTA used (in ml)

E = initial weight (in g)

The degree of purity is calculated with consideration of the corrected calcium oxide content (CaO_{corr}). For this correction the calcium content is reduced by the calcium content in calcium carbonate and calcium sulphite hemihydrate. Pure calcium sulphate dihydrate contains 32.57072787 % CaO.

$$R (\%) = \frac{\text{CaO}_{\text{corr}} \cdot 100}{32.57072787} \left(\frac{\%}{1} \right)$$

3. Thermogravimetric determination of moisture, degree of purity and calcium carbonate content (TGA)

Basics:

With the thermogravimetric analysis (TGA) the loss in weight and/or the bulk change of a sample is measured, which is subjected to a temperature program with a given atmosphere, i.e. the change of the weight of the sample is examined in a thermally controlled environment.

Therefore, commercial equipment is used, which have initial weights in the field of mg or g. With very small initial weights the sample homogeneity is of great importance.

The humidity is determined by drying the gypsum at 40-50 °C up to constant mass.

The degree of purity is calculated from the content of the released crystallization water (KW).

The content of calcium carbonate is calculated with the mass loss caused by the separated carbon dioxide.

Apparatus:

- Thermoanalysis system with evaluation unit
- Aluminium oxide and/or quartz crucible

Reagents:

- Calcium sulphate dihydrate, reagent-grade ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)
- Calcium carbonate, suprapur (CaCO_3)

Procedure:

In micro systems, where only a few mg can be weighed, only residual moisture-free, homogenised gypsum samples are to be used. The original moisture content has to be determined separately.

It is to be proceeded according to the operating instructions. The sample is heated continuously with a rate of approx. 20 K/min or more, depending on the model. A continuous flow of the flushing gas is of great importance.

Test measurements with pure calcium sulphate dihydrate and/or pure calcium carbonate are necessary to examine the system (reference tests). On the basis of these tests the evaluation windows for the determination of the crystallization water content (e.g. 40–360 °C) and/or the CO₂ content (e.g. 620-910° C) can be specified.

It is to be considered that with real samples additional weight deviations may occur, e.g. by organic impurities or sulphites. These arise mainly in the range of 400-550° C.

In the range above 950° C it can possibly come to a desulphurisation of the gypsum and thus to an excess result of the carbonate. Comparative measurements with reference substances and/or other analysis procedures offer security.

It is recommended to analyse and evaluate several initial weights of each sample. Rational procedures result from the use of automatic sample changers.

The respective results for the content of crystallization water and CO₂ are to be averaged and the degree of purity has to be calculated with the following formulas. The calculations and average determination can also be carried out with the device software if possible.

Thermogravimetric macro systems allow analysing several samples at the same time. The operating instructions are to be taken into account.

First of all - on the basis of comparative measurements - the operating temperature programme of the existing equipment has to be tested and modified if necessary. For this, already sufficient analysed real gypsum samples as well as pure substances can be used.

The following temperature programme has proved itself reliable:

proce- dure	cover with/without	heating rate (K/min)	final tep. (°C)	atmosphere	final modus	time excess or % deviation
1	without	12	40	N ₂	constant weight	0,10
2	without	12	360	N ₂	constant weight	0,10
3	without	12	620	N ₂	constant weight	0,10
4	without	12	910	N ₂	constant weight	0,10

The indicated temperatures will be started-up one after another and will be kept constant until all samples get constant weight. In the first step the residual moisture will be removed and in the second step the proportion of crystallization water. Between the third and the fourth step the carbonate will be decomposed.

It is recommended to analyse the sample at least three times. Reference samples should be measured in order to ensure quality assurance.

Sample quantities of 1 - 3 g lead to satisfying test results. Depending on the homogeneity of the test sample the respective sample quantity has to be examined big enough to consider the partial sample representative. A complete crucible filling can lead to long measurement times and/or mismeasurements (decrease findings). It has been proved to

fill the crucible not more than approx. 40 %. Original samples and residual moisture-free samples can both be analysed.

During the evaluation of the weight difference at each temperature step the reference basis is to be taken into account. If original samples were used the results for the portion of crystallization water (difference of weight between 40 and 360° C) as well as the portion of CO₂ (difference of weight between 620 and 910° C) are to be calculated to the residual moisture-free weighted sample.

Modern measuring systems give the opportunity of an individual computation and data output.

Moisture:

The indicated loss in weight at the hold point 40° C is noted, it is equivalent to the moisture (H₂O) in %.

Degree of purity:

The content of crystallization water (difference from loss in weight and/or between 40 and 360° C) can be calculated and plotted by the software of the equipment related to the residual moisture-free weighted sample (KW).

The degree of purity is to be calculated from the content of crystallization water (KW) as follows:

Pure calcium sulphate dihydrate contains 20,927175 % of crystallization water.

$$R^{\circ} (\%) = \frac{KW \cdot 100}{20.927175} \left(\frac{\%}{1} \right)$$

Content of calcium carbonate:

The content of carbon dioxide (difference of loss in weight and/or between 620 and 910° C) can be calculated and plotted by the software of the equipment related to the residual moisture-free weighed sample (CO₂).

The content of calcium carbonate from the content of carbon dioxide is to be calculated as follows (factor: CaCO₃/CO₂ = 2.27421125):

$$\text{CaCO}_3 (\%) = \text{CO}_2 \cdot 2.27421125 (\%)$$

4 Determination of the pH value

The determination procedure follows DIN EN ISO 787-9:1995-04.

Reagents:

- demineralized, CO₂-free water (conductivity < 0.08 μS/cm)
- buffer solution of known pH value

Apparatus:

- pH measuring unit (accuracy: 0.1 unit)
- glass vessel of chemical resistant glass with ground-in glass stopper or rubber stopper

Before the first use the glass vessel is to be sterilized with diluted hydrochloric acid and be thoroughly rinsed with demineralized water. After the materials are poured into the vessel it remains properly closed until the measurement of the pH value.

Procedure:

Add 90 ml of demineralized and CO₂-free water to 10 g ± 0.001 g dry raw gypsum to and stir the 10 % suspension for 1 minute at room temperature. Then leave the suspension for 5 minutes. After separating the sediment (e.g. filtering) the pH value is determined in a clear measuring solution.

Measurement:

Prior to starting the measurement the pH measuring unit is calibrated at room temperature using the buffer solution. Thereafter, determine the pH value of the clear measuring solution. Measure twice and determine the mean pH value, rounded to 0.1 units.

The determination takes place at the dried flue gas desulphurization gypsum. Where a change of the pH value in the drying process cannot be excluded, wet FGD gypsum should be used. This must be noted in the analysis report.

5 Determination of the degree of whiteness / colour of raw gypsum

- degree whiteness as reflectance value R_y ; colour of determination using the numeric colour system

The degree of whiteness is the reflectance value, R_y , of powdery raw gypsum compared with e.g. an enamelled reference tile whose whiteness is referenced to absolute whiteness. Basics of the measuring technology and requirements for white coloured standards are given in DIN 5033-1 to DIN 5033-9.

Measuring procedure:

To determine the degree of whiteness colour measuring instruments working with the spectral process in connection with a white standard (materials, which in its reflexion characteristics are similar or near to that of an ideal reflector $R = 1$ – no absorption). As white standards enamel tiles, pellets made of barium sulphate or sintered PTFE could be used.

For measuring the whiteness degree, the instrument needs to be calibrated to the R_y -value by means of the white standard.

The calibration of the equipments is to be examined before a series of measurements with the white standard.

Procedure:

Approx. 20 g dry, agglomerate-free raw gypsum are shaken by hand in a powder cuvette (diameter: 50 mm, height: 30 mm) until the glass bottom is evenly covered with gypsum. The filling height should be at least 10 mm.

Clean the outer cuvette bottom and check whether the surface is plane. If so, put the cuvette directly onto the colour measuring instrument and measure relative to the white standard. For the operation of the equipment follow the manufacturer's instructions.

Indication of the result of measurement:

The degree of whiteness is exactly indicated to 0.1 %. The reproducibility is depending from the used equipment.

The designation and reflectance value of the white standard are indicated too.

Note:

The determination of the degree of whiteness with different colour measuring instruments may result in different results. Differing results may also be obtained if other white standards, other filters, other light sources or different samples preparations are used.

In many cases the degree of whiteness determined as reflectance value R_y is not sufficient to identify the colour of the raw gypsum. In such cases, measurements based on the numeric colour system (e.g. L, a, b system) are recommended. The procedure and definitions should be agreed between the parties concerned.

6 Determination of the odour - perception

Procedure:

The odour of the sample concerned is determined by comparing it with that of natural gypsum.

7 Determination of screening residues at 32 μm - air-jet screening

The grain or particle size is the diameter of the gypsum particle. The investigation of the residue at 32 μm is described below. The determination of the grain size distribution is described in Annex A7.

Procedure:

Sampling shall be performed in compliance with the regulations as found in the relevant literature and in DIN standards. For the analysis of the residues at 32 μm 50 g \pm 0.1 g of unscreened and dried to constant weight at 40 °C FGD gypsum is placed on a screen with a 0.032 screen mesh bottom according to DIN ISO 3310-1: 2002-09. Insert the test screen into the screening machine (air classifier) and switch the machine on. Choose the screening time such that the residues are not reduced by more than 0.1 % in two successive screenings. Prior to the measurement use a screening time curve to make sure the grains are not comminuted. The residues at 32 μm are given in per cent referred to the quantity of substance put on the screen. The indication of the result is rounded to 1 %.

8 Minor constituents

8.1 Determination of magnesium by AAS as magnesium oxide

– determination by atomic absorption spectrometry (flame AAS)

Basics:

Basis of the procedure is that the elements are able to absorb light of their own emission wavelengths in stimulated condition. The stimulation of the elements takes place by inserting the sample aerosols into an acetylene air and/or acetylene nitrous oxide flame. The detection of the absorption of light takes place by photomultipliers; as radiant source cylindrical cathodes and/or electrodeless discharge lamp are in use.

8.1.1 Magnesium (total)

Reagents:

- standard magnesium solution, β (Mg) = 100 mg/l
- lanthanum oxide solution, ω (La_2O_3) = 5 %:
dilute 50 g lanthanum oxide La_2O_3 in 200 ml hydrochloric acid, $\omega(\text{HCl}) = 16$ %, pour this into a 1000 ml measuring flask, and fill the flask with demineralized water to the mark.
- hydrochloric acid, $\omega(\text{HCl}) = 16$ %:
32% HCl reagent-grade is diluted with demineralized water proportionately 1 to 1

Calibrating solutions:

Dilute the magnesium standard solution to get calibrating solutions with 0.1, 0.2, 0.3, 0.4 and 0.5 mg/l Mg. To 100 ml of each calibrating solution, add 5 ml lanthanum oxide solution and a certain quantity of HCl for adjustment to decomposition solution. A blank solution with 0.0 mg/l Mg is prepared in the same way.

Procedure:

The acid decomposition described in chapter 0.1 is used for the determination of the total magnesium oxide content.

In dependence of the magnesium concentration in the raw gypsum, dilute the A1 stock solution in such a way that its magnesium content is similar to that of the calibrating solutions.

Give the respective A1 stock solution quantity V_0 (e.g. 5 ml or 10 ml) into a 100 ml measuring flask, add 5 ml lanthanum oxide solution and fill up to the mark with demineralized water (= measuring solution).

Measure the calibrating solutions and measuring solution with the AAS as described in the operating instructions (wave length: 285.2 nm).

The obtained Mg concentration β in mg/l is calculated from the difference between the measuring and blank solution. The total MgO content is then calculated as follows (factor: $\text{MgO}/\text{Mg} = 1.65827607$).

Calculation:

$$\text{MgO} (\%) = \frac{\beta \cdot 100 \cdot 0.250 \cdot 1.65827607 \cdot 100}{V_0 \cdot E} \left(\frac{\text{mg} \cdot \text{ml} \cdot \text{l}}{\text{l} \cdot \text{ml} \cdot \text{mg}} \right)$$

The initial weight E is to be given in mg.

8.1.2 Determination of magnesium (water-soluble)

- standard magnesium solution, β (Mg) = 100 mg/l
- lanthanum oxide solution, ω (La_2O_3) = 5 %:
dilute 50 g lanthanum oxide La_2O_3 in 200 ml hydrochloric acid, $\omega(\text{HCl}) = 16$ %, pour this into a 1000 ml measuring flask, and fill the flask with demineralized water to the mark.
- hydrochloric acid, $\omega(\text{HCl}) = 16$ %:
32% HCl reagent-grade is diluted in demineralized water proportionately 1 to 1

Calibrating solutions:

Dilute the standard magnesium solution to get calibrating solutions with 0.1, 0.2, 0.3, 0.4 and 0.5 mg/l Mg. To 100 ml of each calibrating solution, add 5 ml lanthanum oxide solution. A blank solution with 0.0 mg/l Mg is prepared in the same way.

Procedure:

The aqueous extract described in chapter 0.2 and chapter 0.3 respectively is used for the determination of the water-soluble magnesium oxide content.

In dependence of the water-soluble magnesium content in the raw gypsum, dilute the A2 and A3 stock solution respectively in such a way that its magnesium content is similar to that of the calibrating solutions.

Give the respective A2 or A3 stock solution quantity V_0 (e.g. 10 ml) into a 100 ml measuring flask, add 5 ml lanthanum oxide solution and fill up to the mark with demineralised water (= measuring solution).

Measure the calibrating solutions and measuring solution with the AAS as described in the operating instructions (wave length: 285.2 nm).

The obtained Mg concentration β in mg/l is calculated from the difference between the measuring and blank solution. The water-soluble MgO content is then calculated as follows: (factor: $\text{MgO}/\text{Mg} = 1.65827607$):

Calculation:

$$\text{MgO (\%)} = \frac{\beta \cdot 100 \cdot 0.500 \cdot 1.65827607 \cdot 100}{V_0 \cdot E} \left(\frac{\text{mg} \cdot \text{ml} \cdot \text{l}}{\text{l} \cdot \text{ml} \cdot \text{mg}} \right)$$

The initial weight E is to be given in mg.

If the aqueous extract A3 was used, 0.250 l instead of 0.500 l is to be used.

8.2 Determination of sodium by AAS as sodium oxide

– determination by atomic absorption spectrometry (flame AAS)

Basics:

Basis of the procedure is that the elements are able to absorb light of their own emission wavelengths in stimulated condition. The stimulation of the elements takes place by inserting the sample aerosols into an acetylene air and/or acetylene nitrous oxide flame. The detection of the absorption of light takes place by photomultipliers; as radiant source cylindrical cathodes and/or electrodeless discharge lamp are in use.

8.2.1 Sodium (total)

Reagents:

- standard sodium solution, β (Na) = 100 mg/l
- caesium chloride solution, ω (Cs) = 0.5 %:
dissolve 6.335 g CsCl in demineralized water to get 1 l.
- hydrochloric acid, ω (HCl) = 16 %:
32% HCl reagent-grade is diluted in demineralized water proportionately 1 to 1

Calibrating solutions:

Dilute the standard sodium solution to get calibrating solutions with 0.1, 0.3, 0.5 and 1.0 mg/l Na. To 100 ml of each of these calibrating solutions, add 10 ml CsCl to avoid ionization troubles, and a certain amount of HCl for adjustment to the decomposition solution. A blank solution with 0.0 mg/l Na is prepared in the same way.

Procedure:

The acid decomposition described in chapter 0.1 is used for the determination of the total sodium content.

In dependence of the sodium concentration in the raw gypsum, dilute the A1 stock solution in such a way that its sodium content is similar to that of the calibrating solutions. Give the respective A1 stock solution quantity V_0 (e.g. 50 ml) into a 100 ml measuring flask, add 10 ml CsCl solution and fill up to the mark with demineralised water (= measuring solution).

Measure the calibrating solutions and measuring solution with the AAS as described in the operating instructions (wave length: 589 nm).

The obtained Na concentration β in mg/l is calculated from the difference between the measuring and blank solution. The Na_2O content is then calculated as follows (factor: $\text{Na}_2\text{O}/\text{Na} = 1.34796782$).

Calculation:

$$\text{Na}_2\text{O} (\%) = \frac{\beta \cdot 100 \cdot 0.250 \cdot 1.34796782 \cdot 100}{V_0 \cdot E} \left(\frac{\text{mg} \cdot \text{ml} \cdot \text{l}}{\text{l} \cdot \text{ml} \cdot \text{mg}} \right)$$

The initial weight E is to be given in mg.

8.2.2 Sodium (water-soluble)

Reagents

- standard sodium solution, β (Na) = 100 mg/l
- caesium chloride solution, ω (Cs) = 0.5 %:
dissolve 6.335 g CsCl in demineralized water to get 1 l.
- hydrochloric acid, ω (HCl) = 16 %:
32% HCl reagent-grade is diluted in demineralized water proportionately 1 to 1

Calibrating solutions:

Dilute the standard sodium solution to get calibrating solutions with 0.1, 0.3, 0.5 and 1.0 mg/l Na. To 100 ml of each of these calibrating solutions, add 10 ml CsCl to avoid ionization troubles, and a certain amount of HCl for adjustment to the decomposition solution. A blank solution with 0.0 mg/l Na is prepared in the same way.

Procedure:

The aqueous extract described in chapter 0.2 and chapter 0.3 respectively is used for the determination of the water-soluble magnesium oxide content.

In dependence of the sodium concentration in the raw gypsum, dilute the A2 and A3 stock solution respectively in such a way that its sodium content is similar to that of the calibrating solutions.

Give the respective A1 stock solution quantity V_0 (e.g. 50 ml) into a 100 ml measuring flask, add 10 ml CsCl solution and fill up to the mark with demineralised water (= measuring solution).

Measure the calibrating solutions and measuring solution with the AAS as described in the operating instructions (wave length: 589 nm).

The obtained Na concentration β in mg/l is calculated from the difference between the measuring and blank solution. The Na_2O content is then calculated as follows (factor: $\text{Na}_2\text{O}/\text{Na} = 1.34796782$).

Calculation:

$$\text{Na}_2\text{O} (\%) = \frac{\beta \cdot 100 \cdot 0.500 \cdot 1.34796782 \cdot 100}{V_0 \cdot E} \frac{\text{mg}}{\text{l}} \frac{\text{ml}}{\text{ml}} \frac{\text{l}}{\text{mg}}$$

The initial weight E is to be given in mg.

If the aqueous extract A3 was used, 0.250 l instead of 0.500 l is to be used.

8.3 Determination of potassium by AAS as potassium oxide

- determination by atomic absorption spectrometry (flame AAS)

Basics:

Basis of the procedure is that the elements are able to absorb light of their own emission wavelengths in stimulated condition. The stimulation of the elements takes place by inserting the sample aerosols into an acetylene air and/or acetylene nitrous oxide flame. The detection of the absorption of light takes place by photomultipliers; as radiant source cylindrical cathodes and/or electrodeless discharge lamp are in use.

8.3.1 Potassium (total)Reagents

- standard potassium solution, β (K) = 100 mg/l
- caesium chloride solution, ω (Cs) = 0.5 %:
dissolve 6.335 g CsCl in demineralized water to get 1 l.

- hydrochloric acid, $\omega(\text{HCl}) = 16 \%$:
32% HCl reagent-grade is diluted in demineralized water proportionately 1 to 1

Calibrating solutions:

Dilute the standard potassium solution to get calibrating solutions with 0.1, 0.5 and 1.0 mg/l K. To 100 ml of each of these calibrating solutions, add 10 ml CsCl to avoid ionization troubles, and a certain amount of HCl for adjustment to the decomposition solution. A blank solution with 0.0 mg/l K is prepared in the same way.

Procedure:

The acid decomposition described in chapter 0.1 is used for the determination of the total potassium content.

In dependence of the potassium concentration in the raw gypsum, dilute the A1 stock solution in such a way that its potassium content is similar to that of the calibrating solutions.

Give the respective A1 stock solution quantity V_0 (e.g. 50 ml) into a 100 ml measuring flask, add 10 ml CsCl solution and fill up to the mark with demineralised water (= measuring solution).

Measure the calibrating solutions and measuring solution with the AAS as described in the operating instructions (wave length: 766.5 nm).

The obtained K concentration β in mg/l is calculated from the difference between the measuring and blank solution. The K_2O content is then calculated as follows (factor: $\text{K}_2\text{O}/\text{K} = 1.2046048$).

Calculation:

$$\text{K}_2\text{O} (\%) = \frac{\beta \cdot 100 \cdot 0.250 \cdot 1.2046048 \cdot 100}{V_0 \cdot E} \cdot \frac{\text{mg}}{\text{l}} \cdot \frac{\text{ml}}{\text{ml}} \cdot \frac{\text{l}}{\text{mg}}$$

The initial weight E is to be given in mg.

8.3.2 Potassium (water-soluble)

Reagents

- standard potassium solution, $\beta (\text{K}) = 100 \text{ mg/l}$
- caesium chloride solution, $\omega (\text{Cs}) = 0.5 \%$:
dissolve 6.335 g CsCl in demineralized water to get 1 l.
- hydrochloric acid, $\omega(\text{HCl}) = 16 \%$:
32% HCl reagent-grade is diluted in demineralized water proportionately 1 to 1

Calibrating solutions:

Dilute the standard potassium solution to get calibrating solutions with 0.1, 0.5 and 1.0 mg/l K. To 100 ml of each of these calibrating solutions, add 10 ml CsCl to avoid ionization troubles, and a certain amount of HCl for adjustment to the decomposition solution. A blank solution with 0.0 mg/l Na is prepared in the same way.

Procedure:

The aqueous extract described in chapter 0.2 and chapter 0.3 respectively is used for the determination of the water-soluble potassium content.

In dependence of the potassium concentration in the raw gypsum, dilute the A2 and A3 stock solution respectively in such a way that its potassium content is similar to that of the calibrating solutions.

Give the respective A2 or A3 stock solution quantity V_0 (e.g. 50 ml) into a 100 ml measuring flask, add 10 ml CsCl solution and fill up to the mark with demineralised water (= measuring solution).

Measure the calibrating solutions and measuring solution with the AAS as described in the operating instructions (wave length: 766.5 nm).

The obtained K concentration β in mg/l is calculated from the difference between the measuring and blank solution. The K_2O content is then calculated as follows (factor: $K_2O/K = 1.2046048$).

Calculation:

$$K_2O (\%) = \frac{\beta \cdot 100 \cdot 0.500 \cdot 1.2046048 \cdot 100}{V_0 \cdot E} \frac{\text{mg}}{\text{l}} \frac{\text{ml}}{\text{ml}} \frac{\text{l}}{\text{mg}}$$

The initial weight E is to be given in mg.

If the aqueous extract A3 was used, 0.250 l instead of 0.500 l is to be used.

8.4 Determination of aluminium (in total) by AAS as aluminium oxide

- determination by atomic absorption spectrometry (flame AAS)

Basics:

Basis of the procedure is that the elements are able to absorb light of their own emission wavelengths in stimulated condition. The stimulation of the elements takes place by inserting the sample aerosols into an acetylene air and/or acetylene nitrous oxide flame. The detection of the absorption of light takes place by photomultipliers; as radiant source cylindrical cathodes and/or electrodeless discharge lamp are in use.

Reagents

- standard aluminium solution, β (Al) = 1000 mg/l
- caesium chloride solution, ω (Cs) = 0.5 %:
dissolve 6.335 g CsCl in demineralized water to get 1 l.
- hydrochloric acid, ω (HCl) = 16 %:
32% HCl reagent-grade is diluted in demineralized water proportionately 1 to 1

Calibrating solutions:

Dilute the standard aluminium solution to get calibrating solutions with 5, 10, 20, 30, 40 and 50 mg/l Al. To 100 ml of each of these calibrating solutions, add 10 ml CsCl to avoid ionization troubles, and a certain amount of HCl for adjustment to the decomposition solution. A blank solution with 0.0 mg/l Al is prepared in the same way.

Procedure:

The acid decomposition described in chapter 0.1 is used for the determination of the aluminium oxide content.

Give 50 ml stock solution A1 into a 100 ml measuring flask, add 10 ml CsCl solution and fill up to the mark with demineralised water (= measuring solution). Where the aluminium content in the raw gypsum is higher, choose a higher dilution ratio.

Measure the calibrating solutions and measuring solution with the AAS as described in the operating instructions (wave length: 309.3 nm).

The obtained Al concentration β in mg/l is calculated from the difference between the measuring and blank solution. The Al_2O_3 content in the raw gypsum is then calculated as follows (factor $\text{Al}_2\text{O}_3/\text{Al}$: 1.88946373):

Calculation:

$$\text{Al}_2\text{O}_3 (\%) = \frac{\beta \cdot 100 \cdot 0.250 \cdot 1.88946373 \cdot 100}{V_0 \cdot E} \left(\frac{\text{mg} \cdot \text{ml} \cdot \text{l}}{\text{l} \cdot \text{ml} \cdot \text{mg}} \right)$$

The initial weight is to be given in mg.

Note:

Owing to the low sensitivity of aluminium, concentrations below 5 mg/l cannot be reliably determined in the nitrous oxide/acetylene flame. This is to be taken into account in the result.

8.5 Determination of iron (in total) by AAS as iron oxide

- determination by atomic absorption spectrometry (flame AAS)

Basics:

Basis of the procedure is that the elements are able to absorb light of their own emission wavelengths in stimulated condition. The stimulation of the elements takes place by inserting the sample aerosols into an acetylene air and/or acetylene nitrous oxide flame. The detection of the absorption of light takes place by photomultipliers; as radiant source cylindrical cathodes and/or electrodeless discharge lamp are in use.

Reagents

- standard iron solution, β (Fe) = 1000 mg/l
- hydrochloric acid, $\omega(\text{HCl}) = 16 \%$:
32% HCl reagent-grade is diluted in demineralized water proportionately 1 to 1

Calibrating solutions:

Dilute the standard iron solution to get calibrating solutions with 1, 3 and 5 mg/l Fe. To 100 ml of each of these calibrating solutions, add a certain amount of HCl for adjustment to the decomposition solution. A blank solution with 0.0 mg/l Fe is prepared in the same way.

Procedure:

The acid decomposition described in chapter 0.1 is used for the determination of the iron(III) oxide content.

Give 50 ml stock solution A1 into a 100 ml measuring flask and fill up to the mark with demineralised water (= measuring solution). Where the iron(III) oxide content in the raw gypsum is higher, choose a higher dilution ratio.

Measure the calibrating solutions and measuring solution with the AAS as described in the operating instructions (wave length: 248.3 nm).

The obtained Fe concentration β in mg/l is calculated from the difference between the measuring and blank solution. The Fe_2O_3 content in the raw gypsum is then calculated as follows (factor: $\text{Fe}_2\text{O}_3/\text{Fe} = 1.42974483$).

Calculation:

$$\text{Fe}_2\text{O}_3 (\%) = \frac{\beta \cdot 100 \cdot 0.250 \cdot 1.42974483 \cdot 100}{V_0 \cdot E} \left(\frac{\text{mg} \cdot \text{ml} \cdot \text{l}}{\text{l} \cdot \text{ml} \cdot \text{mg}} \right)$$

The initial weight E is to be given in mg.

8.6 Determination of manganese (water-soluble) by AAS as manganese oxide

– determination by atomic absorption spectrometry (flame AAS)

Basics:

Basis of the procedure is that the elements are able to absorb light of their own emission wavelengths in stimulated condition. The stimulation of the elements takes place by inserting the sample aerosols into an acetylene air and/or acetylene nitrous oxide flame. The detection of the absorption of light takes place by photomultipliers; as radiant source cylindrical cathodes and/or electrodeless discharge lamp are in use.

Reagents:

– standard manganese solution, $\beta(\text{Mn}) = 1000 \text{ mg/l}$

Calibrating solutions:

Dilute the standard manganese solution to get calibrating solutions with 1, 3 and 5 mg/l Mn. A blank solution with 0.0 mg/l Mn is prepared in the same way.

Procedure:

The aqueous extract described in chapter 0.2 and chapter 0.3 respectively is used for the determination of the water-soluble manganese content.

Give 50 ml stock solution A2 and A 3 respectively into a 100 ml measuring flask and fill up to the mark with demineralised water (= measuring solution). Where the manganese content in the raw gypsum is higher, choose a higher dilution ratio.

Measure the calibrating solutions and measuring solution with the AAS as described in the operating instructions (wave length: 279.8 nm).

The obtained Mn concentration β in mg/l is calculated from the difference between the measuring and blank solution. The MnO content in the raw gypsum is then calculated as follows (factor: $\text{MnO}/\text{Mn} = 1.291226235$).

Calculation:

$$\text{MnO (\%)} = \frac{\beta \cdot 100 \cdot 0.500 \cdot 1.291226235 \cdot 100}{V_0 \cdot E} \left(\frac{\text{mg} \cdot \text{ml} \cdot \text{l}}{\text{l} \cdot \text{ml} \cdot \text{mg}} \right)$$

The initial weight E is to be given in mg.

If the aqueous extract A3 was used, 0.250 l instead of 0.500 l is to be used.

8.7 Determination of magnesium, sodium, potassium, aluminium, iron and manganese by means of inductive coupled plasma (ICP) OES as oxides

Basics:

Basis of the procedure is the measurement of the emitted light of the elements to be determined after stimulation by means of inductive coupled plasma (ICP-OES) by optical spectrometric detection.

Malfunctions:

Different kinds of malfunctions can contribute to mistakes regarding the determination. They can be summarized as follows (excerpt of the DIN EN ISO 11885; 1998-04).

Spectral malfunctions:

- Line coincidences; these effects are compensated by using computer-controlled corrections of the raw data.
- Band coincidences; these can be compensated by choosing of another wave length.

Background malfunctions:

- Background contribution of continuous recombination phenomenon of the plasma.
- Background contribution by scattered light of band emission of elements, which are present in higher concentration.

Usually the impact of an underground malfunction can be compensated by underground correction.

During the investigation of an unusual sample matrix the sample will be measured in different dilutions, as far as the concentration of the determined element permits, and/or if possible, will be examined for plausibility with other analysis techniques (e.g. AAS, RFA).

Equipment:

- Inductive coupled plasma (ICP-OES) with auto sampler
- Pipettes with different volume
- Divers flasks
- Auto sampler vials

Reagents:

- multi-standard aluminium solution, ($\beta(\text{Mg, K, Al, Fe, Mn}) = 1,000 \text{ mg/l}$) or if necessary single element standards, which are suitable for ICP-OES
- hydrochloric acid, $\omega(\text{HCl}) = 16 \%$:
32% HCl reagent-grade is diluted in demineralized water proportionately 1 to 1

Multi-element calibration solutions:

Element / Concentration	Magnesium (mg/l)	Sodium (mg/l)	Potassium (mg/l)	Aluminium (mg/l)	Iron (mg/l)	Manganese (mg/l)
Blank solution	0	0	0	0	0	0
Standard 1	0.1	0.1	0.1	0.5	0.1	0.1
Standard 2	0.5	0.5	1.0	25.0	5.0	5.0
Standard 3	1.0	1.0	2.0	50.0	10.0	10.0
Control sample	0.5	0.5	0.5	25	5	1.0

The concentrations of the multi-element standards necessary for the calibration must correspond to the conditions in the digesting solution (chapter 01) and/or the aqueous extracts (chapter 02 or 03). The concentration mentioned above are exemplary and should be adapted according to the own requirements.

The single standard solutions are to be adapted according to the acid decomposition with hydrochloric acid (30 ml HCl auf 250 ml) as in chapter 01. The adoption does not take place for the aqueous extracts (02 or 03).

The control sample should not be identical to the calibration sample!

Procedure:

The acid decomposition according to chapter 01 is used for the determination of the total contents of the elements mentioned above. The aqueous extract according to chapter 02 and chapter 03 respectively is used for the determination of the water-soluble contents.

The following wave lengths can be used for the individual determinations:

Element	Magnesium (nm)	Sodium (nm)	Potassium (nm)	Aluminium (nm)	Iron (nm)	Manganese (nm)
Wave length	279.079	589.592	766.490	308.215	259.940	257.610
Wave length	279.553	588.995	-	396.152	238.20	260.568
Wave length	285.213	330.237	-	167.08	-	-

The ICP OES equipment is to be put into operation following the manufacturer's instructions. The calibration samples (standards), control samples and measuring solutions are measured in accordance to operating instructions (or testing instruction).

The obtained element concentrations β in mg/l is calculated from the difference between the measuring and blank solution. The element oxid content in the raw gypsum is then calculated for the individual elements.

Calculation:

Regarding the calculation the following factors have to be taken into account:

Element		Element oxide	Factor
Magnesium	→	Magnesium oxide (MgO)	1.65827607
Sodium	→	Sodium oxide (Na ₂ O)	1.34796782
Potassium	→	Potassium oxide (K ₂ O)	1.2046048
Aluminium	→	Aluminium oxide (Al ₂ O ₃)	1.88946373
Iron	→	Iron oxide (Fe ₂ O ₃)	1.42974483
Manganese	→	Manganese oxide (MnO)	1.291226235

Example:

MgO from the acid decomposition A1 and the aqueous extract A3 respectively. If the aqueous extract A2 was used, 0.500 l instead of 0.250 l is to be used.

$$\text{MgO (\%)} = \frac{\beta \cdot 100 \cdot 0.250 \cdot 1.65827607 \cdot 100}{V_0 \cdot E} \left(\frac{\text{mg} \cdot \text{ml} \cdot \text{l}}{\text{l} \cdot \text{ml} \cdot \text{mg}} \right)$$

The initial weight E is to be given in mg.

8.8 Determination of chloride**8.8.1 Potentiometric**Determination of chloride in band filter gypsum (Potentiometric method with titrator)

Give 5 bis 10 g ± 0,01 g gypsum into a 100 ml beaker, fill demineralized water up to the 20 ml mark and then with glacial acetic acid up to the 100 ml mark. The Ag titrode and the dosage tube will be rinsed off with demineralized water and dived into the beaker. The magnetic stirrer should be stirred with a speed of approx. 500 U/min. The appropriate measuring method for chloride is to be preselected and the program is to be started after the input of the weighted gypsum mass. The content of chloride is to be given in mg/kg. Thus, the chloride blank value of the acetic acid has to be taken into account.

8.8.2 Ionic-chromatographicBasics:

DIN EN ISO 10304-1:1995-04 Determination of the dissolved anions by means of ionic-chromatography, procedure for low contaminated water

DIN EN ISO 10304-2:1996-11 Determination of dissolved anions by means of ionic-chromatography, determination in waste water

The anions are liquid-chromatographically separated by means of a separating column. The stationary phase is an anion exchanger with low capacity. For the mobile phase (eluent) aqueous solutions of salts of weak mono- and dibasic acids are basically possible.

Equipment:

- Ionic-chromatographic system
- Micro litre pipettes
- Injection header filter, 0,45 µm pore size

Reagents:

- demineralized water (water must have an electrical conductivity of < 0,08 µS/cm and does not contain particles > 0,45 µm)
- eluent (degassed)
- anion standard solutions
- helium
- nitrogen

Preparation and execution of samples:

The ionic chromatograph is to be put into operation according to the manufacturer's information. The operating state is given if the base line is stable.

The calibration solutions are synthesized by diluting the anion standard solutions for the expected range.

At first the systems with at least five calibration solutions is calibrated and the calibration is examined by means of the AQA¹ standard. For the production of the AQA solution other standard solutions have to be used when producing calibration solutions. Subsequently, the samples are measured.

The sample solutions are diluted in such a way that the concentrations are within the calibration range. An injection header filter should be up-stream when injecting into the IC system.

Evaluation:

The anions are identified by comparison of the retention times of the sample with those of the calibration solutions. The surfaces or heights of the signal peaks are in proportion to the concentrations of the anions.

Indication of results:

The indication of the results takes place related to the weighed gypsum in mg/kg. At the most three significant places are indicated.

Quality-assurance measures

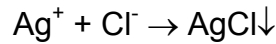
- Control standard: Daily examination with control standard in the field of work.
Piston pipette: Examination in accordance with manufacturer data.

¹ AQA = Analytical Quality Assurance

8.8.3 Titrimetric

Basics:

Chloride ions together with silver ions form hardly soluble silver chloride.



Reagents:

- silver nitrate solution, $c(\text{AgNO}_3) = 0,01 \text{ mol/l}$
- ammonium thiocyanate, $c(\text{NH}_4\text{SCN}) = 0,01 \text{ mol/l}$
- indicator solution:
A saturated iron(III) ammonium sulphate solution is added to nitric acid until the vanishing of brown colouring.
- nitric acid, $\omega(\text{HNO}_3) = 32,5\%$:
65% HNO_3 reagent-grade is diluted in demineralized water proportionately 1+1

Procedure:

Give $10 \text{ g} \pm 0,1 \text{ g}$ dried raw gypsum into a 400 ml beaker with 10 ml silver nitrate solution (V_1 = submitted silver nitrate solution in ml), 50 ml nitric acid and 75 ml demineralized water and heat it up to approx. $80 \text{ }^\circ\text{C}$ while mixing it approx. 5 minutes. Then add 100 ml boiling demineralized water and mix it further five minutes at $80 \text{ }^\circ\text{C}$. After the cooling the solution is filtered out via a nutsch filter and is rewashed with hot demineralized water. The entire filtrate is added with 2 ml indicator solution and titrated with ammonium thiocyanate solution up to the colour change from colourless to red (V_2 = used ammonium thiocyanate solution in ml). 1 ml used silver nitrate solution is equivalent to 0.35453 mg chloride.

Calculation:

$$\text{Cl}^- \text{ (mg / kg)} = \frac{(V_1 - V_2) \cdot 0.35453 \cdot 1000}{E} \left(\frac{\text{mg} \cdot \text{ml}}{\text{ml} \cdot \text{kg}} \right)$$

The initial weight E is to be given in g.

8.9 Determination of sulphur dioxide (SO₂) as calcium sulphite-hemihydrate - titrimetric with iodine

Reagents:

- iodine solution, $c(\text{I}_2) = 0.05 \text{ mol/l}$:
12.690 g Iod are dissolved in demineralized water to get 1 l.
- sodium thiosulfate solution, $c(\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}) = 0.1 \text{ mol/l}$:
24.818 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ are dissolved in demineralized water to get 1 l.
- starch solution:
Dissolve 10 g soluble starch in 500 ml boiling demineralized water and let the solution cool down.
- sulfuric acid, $\omega(\text{H}_2\text{SO}_4) = 48 \%$:
96%ige H_2SO_4 reagent-grade is diluted in demineralized water proportionately 1 to 1.

Procedure:

Give $1 \text{ g} \pm 0,0005 \text{ mg}$ dry raw gypsum (E = initial weight in g) into a titration vessel with the iodine solution in excess (V_1 = submitted iodine solution in ml), add 50 ml demineralized water, 5 ml sulphuric acid and 1 to 3 ml starch solution. The excessive iodine solution is titrated back with the sodium thiosulfate solution up to the colour change from blue to colourless (V_2 = used sodium thiosulfate solution in ml). 1 ml used iodine solution is equivalent to $3.203 \cdot 10^{-3} \text{ g SO}_2$ (factor: $\text{CaSO}_3 \cdot \frac{1}{2} \text{H}_2\text{O} / \text{SO}_2 = 2.0161$).

Calculation

$$\text{CaSO}_3 \cdot \frac{1}{2} \text{H}_2\text{O} (\%) = \frac{3.203 \cdot 10^{-3} \cdot (V_1 - V_2) \cdot 2.0161 \cdot 100}{E} \left(\frac{\text{g} \cdot \text{ml}}{\text{ml} \cdot \text{g}} \right)$$

The initial weight E is to be given in g.

Note:

It is recommended to carry out the oxidation with iodine in a closed vessel.

8.10 Determination of oxidable constituents as C, such as organic matter, soot, fly coke (C_{coke}) - selective determination with a carbon analyzer

Basics:

After the elimination of the inorganic carbon (C_{CaCO_3}) the carbon consisting of coke particles (C_{coke}) is selectively determined with a carbon analyzer.

Reagents:

– hydrochloric acid reagent-grade, $\omega(\text{HCl}) = 32 \%$

Procedure:

$10 \text{ g} \pm 0.0005 \text{ g}$ dry raw gypsum (E = initial weight in g) are suspended in a 250 ml beaker (wide-necked) with 15 ml demineralized water.

Stir constantly (magnetic stirrer) and heat up to approx. $60 \text{ }^\circ\text{C}$, then add HCl drop by drop until no more CO_2 generated.

Stir the suspension at approx. $60 \text{ }^\circ\text{C}$ 15 minutes by adding 1 ml HCl and after cooling filter it out via a membrane filter (pore size $0.45 \text{ } \mu\text{m}$). Possible caking on the damp membrane filter is to be removed by rinsing with demineralized water and/or with a rubber wiper.

After drying the residue (A = final weight in g) is weighed, homogenized in mortar and the relative content of C_{coke} is threefoldly determined with a C analyzer. The initial weight of the sample depends on the content of the C_{coke} sample.

The C analyzer is calibrated by means of a calcium sulphate calcium carbonate standard, which was generated by measuring calcium carbonate (a C_{coke} calcium sulphate standard is not available). Thus, at least threefold determinations are carried out by two different initial weights. The initial weights are selected in such a way that the measuring range of the samples to be analysed is covered.

Calculation:

$$C_{\text{coke}} (\%) = C_{\text{coke rel.}}(\%) \cdot \frac{A}{E} \left(\frac{\text{g}}{\text{g}} \right)$$

The initial weight is to be given in g.

Indication of result of measurement:

The result of measurement is given to approx. 0.01 %.

Note:

Concerning the content of $C_{\text{coke}} > 0.1$ % the raw gypsum has to be mortared and homogenized.

8.11 Determination of „HCl-insolubles“ - gravimetric

HCl insolubles are the substances left over from the acid decomposition of gypsum (residues) as described in chapter 0.1. The flue dust part is covered (more or less) in „HCl insolubles“.

Reagents:

- hydrochloric acid, $\omega(\text{HCl}) = 16$ %:
32% HCl reagent-grade is diluted in demineralized water proportionately 1 to 1

Procedure:

Give approx. $1 \text{ g} \pm 0.1 \text{ mg}$ dry raw gypsum ($E =$ initial weight in g) into a beaker, add some 30 ml hydrochloric acid and some 120 ml hot demineralized water. Keep this mixture at the boil for about 10 minutes, filter it off through an applicable filter, e.g. membrane filter and rewash with hot demineralized water. Slowly incinerate the filter with the residues in a crucible, and ignite at 1000 °C. Let the residues cool off in a desiccator, then weigh ($A =$ final weight in g).

Calculation:

$$\text{HCl-insolubles} (\%) = \frac{A \cdot 100}{E} \left(\frac{\text{g}}{\text{g}} \right)$$

The initial weight E is to be given in g

8.12 Determination of carbonates as calcium carbonate**8.12.1 Acidimetric**Basics:

The determination is based on an indirect acidimetric measurement. H_2O_2 is added to avoid faults that may be caused by sulphite.

The method is applicable to carbonate contents of 0.1 to 2 %. The measuring range can be increased by increasing the acid quantity or acid concentration.

Reagents:

- hydrochloric acid, $c(\text{HCl}) = 0.1 \text{ mol/l}$
- sodium hydroxide solution, $c(\text{NaOH}) = 0.1 \text{ mol/l}$
- hydrogen peroxide, $\omega(\text{H}_2\text{O}_2) = 3 \%$
- tashiro indicator:
Alcoholic methyl red solution and 0.1 % methylene blue solution or methyl orange solution.

Procedure:

Give $1 \text{ g} \pm 0.0005 \text{ mg}$ dry raw gypsum (E = initial weight in g) into a 400 ml beaker, and add approx. 10 ml demineralized water and a few drops of H_2O_2 . After about 2 minutes, add 20 ml hydrochloric acid, let it react for a short time, then add approx. 20 ml demineralized water (V_1 = provided hydrochloric acid). Heat up this sample for approx. 15 minutes to 50 up to 70 °C. Let the solution cool down, then add approx. 200 ml demineralized water and stir for some 5 min. Thereafter, titrate back the excess hydrochloric acid with sodium hydroxide solution up to colour change of the used indicator or by using a titrator up to pH 7 (V_2 = used sodium hydroxide). 1 ml hydrochloric acid used is equivalent to $2.2005 \cdot 10^{-3} \text{ g CO}_2$ (factor: $\text{CaCO}_3/\text{CO}_2 = 2.27421125$).

Calculation

$$\text{CaCO}_3 (\%) = \frac{2.2005 \cdot 10^{-3} \cdot (V_1 - V_2) \cdot 100}{E} \left(\frac{\text{g} \cdot \text{ml}}{\text{ml} \cdot \text{g}} \right)$$

The initial weight E is to be given in g.

8.12.2 Thermogravimetric

See TGA-Method in current number 3.

9 Determination of trace elements

The determination of the trace elements can be accomplished e.g. by means of AAS or ICP-OES. According to chapter 04 the microwave decomposition is used for the determination of trace elements. The dilution of the master solution A4 is to be selected according to the trace element concentration in the raw gypsum in such a way that its concentration is in the range of the calibration solutions.

Instead of the microwave decomposition the pressure composition for electrostatic filter ashes (E filter dust) and coarse ashes with nitric acid/hydrofluoric acid according to the VGB Analyses Sheet 4.4.1.1 according to the alternations part 11.3 (initial weight of the sample 1 g, 10 ml nitric acid, 1 ml hydrofluoric acid, duration of decomposition 4 h) can be analogically carried out.

Part 2 Annex to analysis methods

This collection of additional analytical methods is meant to supplement the reference analytical methods of Part I. It's a collection of proven test procedures for FGD gypsum analyses which are suitable for internal routine quality testing purposes. The collection do not claim to be complete.

For some analytical methods, special measuring instruments are required which save a lot of time in routine analyses.

The measuring methods referred to as indirect deliver no quantitative data; however, they are suitable for qualitative evaluations.

Prefixed by the letter "A", the numbers of the individual methods in this part are the same as those in Part I.

	Page	
A 5	Determination of degree of whiteness / of colour of raw gypsum	33
A 7	Determination of particle size distribution by laser granulometry	33
A 8	Other constituents	34
A 8.8	Photometric determination of chloride	34
A 8.10	Technological examination of gypsum binders	35
A 8.12	Determination of carbonates as calcium carbonate (indirect inorganic determination of carbon)	36
A 8.13	Determination of reactivity of limestone	37

A 5 Determination of degree of whiteness / of colour of raw gypsum

Different readings may be obtained when the degree of whiteness is measured with different colour measuring instruments. This is due to the use of different optical systems (light incidence angle, filter, light type), different calibration standards and different ways of sample preparation (powder or pressed parts).

Discrepancies also result from the use of a non-unified nomenclature and several colour systems (Cielab system, NCS colour system standard colour values X, Y, Z, etc.).

In cases of doubt, it is recommended to consult the relevant DIN standards, such as:

DIN 5033	Colour measurement
DIN 53163	Determination of the lightness of extenders and white pigments in powder form
DIN 55980	Determination of hue of near white specimens
DIN 55981	Determination of the relative hue of near white specimens
DIN 6174	Colorimetric determination of chromaticity and colour differences in the approx. uniform CIELAB colour space
DIN 55600	Determination of significance of colour differences with surface colours according to the CIELAB formula ¹

Most of the instruments for analysis can also be used for colour measurements to the L, a, b system which allows the hue, brightness and saturation of a colour (and thus the impression the human eye gets of it) to be accurately described. In the system, "L" stands for brightness (white-black axis), whereas "a" and "b" stand as well for hue as for saturation, respectively. "a" and "b" define the position on 2 colour axes, with "a" being assigned to the red-green axis and "b" to the yellow-blue axis.²

A 7 Determination of particle size distribution by laser granulometry

The grain or particle size is the diameter of a particle. Since, as a rule, flue gas gypsum particles are not of a spherical shape, the particle diameters measured can only be considered to be equivalent values.

The particle size distribution is determined on the basis of particle characteristics. Different size distributions will be obtained when different particle size measuring systems are used.

Basics:

Diffraction of the coherent light beam of a He-Ne laser by the grains of the sample is analyzed.

The particle size is derived from the distribution of the light energy across the focal plane of an optical system which is determined by means of a multicell detector. Because of the water solubility of gypsum, use isopropanol as suspending medium.

¹ L, a, b system

² Literature: Brochure of company Minolta "Exact Colour Communication" from March 1984

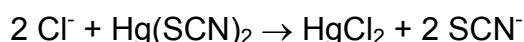
A 8 Other constituents

A 8.8 Photometric determination of chloride

This determination is carried out following DIN 51727: 2001-06, examination of solid fuels – determination of chloride content.

Basics:

Chloride ions react with mercury(II) thiocyanate to undissociated mercury chloride and thiocyanate ions.



The thiocyanate ions together with the iron(III) ions form orange coloured iron(III) thiocyanate whose colouring is measured by photometry.

Reagents:

- hydrogen peroxide solution, $\omega(\text{H}_2\text{O}_2) = 10 \%$
- iron(III) ammonium sulphate solution:
120 g $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ are dissolved in 1000 ml nitric acid, $c(\text{HNO}_3) = 9 \text{ mol/l}$
- mercury(II) thiocyanate solution:
Approx. 0.3 g $\text{Hg}(\text{SCN})_2$ are dissolved in 100 ml ethanol, $\omega(\text{C}_2\text{H}_5\text{OH}) = 95 \%$
- chloride solution 1:
0.3298 g at $105 \pm 2 \text{ }^\circ\text{C}$ dried NaCl are dissolved in 1000 ml demineralized water. 1 ml of this solution contains 0.200 mg chloride.
- chloride solution 2:
25 ml of the chloride solution 1 are diluted with demineralized water to 200 ml. 1 ml of this solution contains 0.025 mg chloride.

Procedure:

For the determination of the chloride content the aqueous excerpt is used according chapter 0.2 and chapter 03 respectively.

An exactly measured volume V_0 (e.g. 10 ml) of the master solution A2 and A3 respectively is given in a 100 ml volumetric flask and is diluted to approx. 50 ml (measuring solution). Depending on the content of chloride the gypsum sample V_0 is chosen in such away that its content is in the range of the calibration solutions.

In each case 1 ml, 2 ml, 4 ml, 6 ml, 8 ml and 10 ml of the chloride solution 2 are in a 100 ml volumetric flask. It is diluted to approx. 50 ml in each case.

The calibration solutions contain 0,025 mg, 0.05 mg, 0.1 mg, 0.15 mg, 0.2 mg and 0.25 mg of chloride. A blind solution is manufactured with demineralized water, only.

To these already prepared solutions (calibration solutions, blind solutions, measuring solutions) are successively given:

- 1 ml H_2O_2 solution
- 10 ml $\text{NH}_4\text{Fe}(\text{SO}_4)_2$ solution
- 10 ml $\text{Hg}(\text{SCN})_2$ -solution

Subsequently, they are to be filled up to the mark.

After a holding time of 10 minutes (must be kept) the solutions are measured in the filter photometer in vessels of 2 cm at 436 nm in comparison to demineralized water.

Evaluation:

In each case the extinction of the blind value is subtracted from the extinction of the calibration solutions. Afterwards the regression line is calculated by the calibration points and the zero-point. The correlation coefficient should be $> 0,999$.

The chloride mass $m(\text{Cl}^-)$ in mg result from the regression line and from the corrected extinction value.

Calculation:

$$\text{Cl}^- (\text{mg} / \text{kg}) = \frac{m(\text{Cl}^-) \cdot 500 \cdot 10^6}{V_0 \cdot E} \left(\frac{\text{mg} \cdot \text{ml} \cdot \text{mg}}{\text{ml} \cdot \text{mg} \cdot \text{kg}} \right)$$

The initial value E is to be given in mg.

If the aqueous extract A3 is used 250 ml instead of 500 ml are to be used.

Note:

Rapid tests are available on the market, which clearly reduce the chemical expenditure and thus, simplify the problem of disposal.

A 8.10 Technical examination of gypsum binders

Basics:

Organic constituents from additives, which are added into flue gas cleaning plants in order to separate either NO_x simultaneously or to increase the absorbency for SO_2 – for example polycarboxylic acids – influence the quality of burnt FGD gypsum as well as the technological characteristics regarding processing. In the context of an indirect method the examinations on stucco (from FGD gypsum) as gypsum binder are carried out according to DIN EN 13279-1: 2008-11, Number 3.2 and 5.3 (Table 3).

Procedure:

According to the test specifications of the DIN EN 13279-2: 2004-10 stucco (made from FGD gypsum) is examined regarding hardening time and mechanical properties as bending tensile strength, compressive strength or surface hardness.

Evaluation:

The quality requirements – listed in DIN EN 13279-1: 2008-11 Gypsum binders and dry gypsum mortar – Part 1: Terms and requirements - may not be unfavourably affected regarding time for hardening (begin and end of hardening), bending tensile strength and surface hardness. Furthermore, the end of hardening shall not exceed 60 minutes.

A 8.12 Determination of carbonates as calcium carbonate (indirect inorganic determination of carbon)

Basics:

The inorganic carbon (C_{CaCO_3}) is determined as the difference between the total carbon content (C_{total}) and the carbon consisting of coke particles (C_{coke}). C_{total} and C_{coke} are selectively measured with a carbon analyzer.

Reagents:

– hydrochloric acid, ω (HCl) = 32 %

Procedure:

Give 10 g \pm 0.1 mg dry raw gypsum (E = initial weight in g) into a 250 ml beaker (wide-necked), and suspend in 15 ml demineralized water.

While stirring the suspension constantly with a magnetic stirrer and heating it to approx. 60 °C, add HCl drop by drop until CO₂ is no longer generated.

Add 1 ml HCl, then stir the suspension for 15 minutes at approx. 60 °C, and filter off after cooling down through a membrane filter (pore size 0.45 μm). Remove any baked-on material from the wet membrane filter by rinsing with demineralized water or by means of a rubber wiper.

After drying the residue weigh it (A = final weight in g), homogenize it in a mortar, and determine the relative C_{coke} content. Subsequently, the C_{total} content is determined from the dry raw gypsum.

The C-analyzer is calibrated by means of a calcium sulphate / calcium carbonate standard, which was generated by measuring calcium carbonate.

At least triple determinations from the standard sample are carried out with two different initial weights. The initial weights are selected in such a way that the measuring range of the samples to be analysed is covered.

Evaluation:

The content of C_{CO_2} (factor: $\text{CaCO}_3/\text{C} = 8.33314461$) is determined as the difference between the content of C_{total} and the content of C_{coke} relating to initial weight:

$$C_{\text{coke}} (\%) = C_{\text{coke rel.}} (\%) \cdot \frac{A}{E} \left(\frac{\text{g}}{\text{g}} \right)$$

The initial weight E is given in g.

$$C_{\text{CO}_2} (\%) = C_{\text{total}} (\%) - C_{\text{coke}} (\%)$$

$$\text{CaCO}_3 (\%) = C_{\text{CO}_2} (\%) \cdot 8.33314461$$

Note:

At C_{coke} contents of > 0.1 %, the raw gypsum has to be ground in a mortar and homogenized.

A 8.13 Determination of reactivity of limestone

Basics:

The dissolving rate of limestone powder compared with acids (1mol/l HCl) can be determined by the titrimetric procedure at constant pH value (4,5) and at a temperature of 20 °C.

Reagents:

– hydrochloric acid; c (HCl) = 1 mol/l

Procedure:

Add 0.5 g ± 0.0005 g limestone powder (E = initial weight) in a 250 ml beaker (long-necked) with 200 ml demineralized water and suspend it by means of a magnetic stirrer. This stirrer should run with high speed if possible. Before the titration stir it 2 minutes, the ph value amounts to 9 – 9.5 and will be measured by means of a glass electrode. The titration starts with simultaneous time measurement, whereby the consumption will be read or a pen recorder charts the consumption versus time. Regarding the evaluation the volumes of the used hydrochloric acid are noted, which are necessary

a) to reach the final ph value: V_1

b) after 1 minute: V_2

c) after 5 minutes: V_3

d) after 25 minutes: V_4

The investigation is to be accomplished via repeat determination. The maximum metering rate of the burette or of the titration automat should be approx. 30 ml/min. The speed of titration will be reduced at pH <5. The titration end point will be achieved at pH 4.5. 1 ml of the used hydrochloric acid is equivalent to $22.00475 \cdot 10^{-3}$ g CO_2 (factor: $\text{CaCO}_3/\text{CO}_2 = 2.27421125$).

Calculation:

$$\text{CaCO}_3 (\%) = \frac{22.00475 \cdot 10^{-3} \cdot V_x \cdot 2.27421125 \cdot 100}{E} \left(\frac{\text{g} \cdot \text{ml}}{\text{ml} \cdot \text{g}} \right)$$

The initial weight E is given in g.

Thereby, it is assumed that the limestone powder sample is approx. 100 % CaCO_3

Evaluation:

On the basis of a diagram the limestone reactivity can be assessed – rate of CaCO_3 (%) versus time.

Part 3 Chemical/physical tables for the determination of gypsum parameters

	Page
(I) International atomic weights	39
(II) Chemical formulas and molecular weights of essential compounds related to gypsum	42
(III) Conversion factors for flue gas desulphurization processes	43
(IV) Characteristics of the phases in the system $\text{CaSO}_4/\text{H}_2\text{O}$	45

(I) International atomic weights

The absolute atomic mass (unit: u), the relative atomic mass (without unit) and the molecular atomic mass (unit: g/mol) have the same numerical value. The atomic mass unit u is equivalent to 1/12 of the atomic mass of the carbon isotope ^{12}C ($1 \text{ u} = 1.66056 \cdot 10^{-24} \text{ g}$).

Element	Symbol	Atomic number	Atomic weight ²
Actinium	Ac	89	[227]
Aluminium	Al	13	26.9815386
Americium	Am	95	[243]
Antimony	Sb	51	121.76
Argon	Ar	18	39.948
Arsenic	As	33	74.9216
Astatine	At	85	[210]
Barium	Ba	56	137.327
Berkelium	Bk	97	[247]
Beryllium	Be	4	9.012182
Bismuth	Bi	83	208.9804
Bohrium	Bh	107	[272]
Boron	B	5	10.811
Bromine	Br	35	79.904
Cadmium	Cd	48	112.411
Calcium	Ca	20	40.078
Californium	Cf	98	[251]
Carbon	C	6	12.0107
Cerium	Ce	58	140.116
Cesium	Cs	55	132.905452
Chloride	Cl	17	35.453
Chrom	Cr	24	51.9961
Cobalt	Co	27	58.933195
Copper	Cu	29	63.546
Curium	Cm	96	[247]
Darmstadtium	Ds	110	[281]
Dubnium	Db	105	[268]
Dysprosium	Dy	66	162.5
Einsteinium	Es	99	[252]
Erbium	Er	68	167.259

¹ The [Commission on Isotopic Abundances and Atomic Weights](#) (II.1) met in Pisa, Italy, prior the 44th IUPAC General Assembly held in Torino, Italy, 4-12 August 2007. Following its meeting, the Commission recommended significant changes to the standard atomic weights, $A_r(E)$, of 5 chemical elements. The following changes are based on new determinations of isotopic abundances and reviews of previous isotopic abundances and atomic masses:

	From	To
lutetium	174.967(1)	174.9668(1)
molybdenum	95.94(2)	95.96(2)
nickel	58.6934(2)	58.6934(4)
ytterbium	173.04(3)	173.054(5)
zinc	65.409(4)	65.38(2)

The values are presented in a concise notation whereby the standard uncertainty is given in parenthesis next to the least significant digits to which it applies; for example, $A_r(\text{Zn}) = 65.38(2)$ is the concise form of the expression $A_r(\text{Zn}) = 65.38 \pm 0.02$. In addition, the recommended value for the isotope amount ratio of $^{40}\text{Ar}/^{36}\text{Ar}$, which may be of importance to geochronologists, has been changed from 296.03(53) to 298.56(31).

These changes will be published in a new Table of Standard Atomic Weights 2007, which will be submitted for publication in *Pure and Applied Chemistry* by the end of 2007.

² Der Wert in eckigen Klammern, wie z.B. [227], gibt die Atommasse des langlebigsten Isotops des betreffenden Elements an, da das Element keine stabilen Nuklide hat.

Element	Symbol	Atomic number	Atomic weight ¹
Europium	Eu	63	151.964
Fermium	Fm	100	[257]
Fluorine	F	9	18.9984032
Francium	Fr	87	[223]
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69.723
Germanium	Ge	32	72.64
Gold	Au	79	196.966569
Hafnium	Hf	72	178.49
Hassium	Hs	108	[270]
Helium	He	2	4.002602
Holmium	Ho	67	164.93032
Hydrogen	H	1	1.00794
Indium	In	49	114.818
Iodine	I	53	126.90447
Iridium	Ir	77	192.217
Iron	Fe	26	55.845
Krypton	Kr	36	83.798
Lanthanum	La	57	138.90547
Lawrencium	Lr	103	[262]
Lead	Pb	82	207.2
Lithium	Li	3	6.941
Lutetium	Lu	71	174.9668
Magnesium	Mg	12	24.305
Manganese	Mn	25	54.938045
Meitnerium	Mt	109	[276]
Mendelevium	Md	101	[258]
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.96
Neodymium	Nd	60	144.242
Neon	Ne	10	20.1797
Neptunium	Np	93	[237]
Nickel	Ni	28	58.6934
Niobium	Nb	41	92.90638
Nitrogen	N	7	14.0067
Nobelium	No	102	[259]
Osmium	Os	76	190.23
Oxygen	O	8	15.9994
Palladium	Pd	46	106.42
Phosphor	P	15	30.973762
Platinum	Pt	78	195.084
Plutonium	Pu	94	[244]
Polonium	Po	84	[209]
Potassium	K	19	39.0983
Praseodymium	Pr	59	140.90765

¹ Der Wert in eckigen Klammern, wie z.B. [257], gibt die Atommasse des langlebigsten Isotops des betreffenden Elements an, da das Element keine stabilen Nuklide hat.

Element	Symbol	Atomic number	Atomic weight ¹
Promethium	Pm	61	[145]
Protactinium	Pa	91	231.03588
Radium	Ra	88	[226]
Radon	Rn	86	[222]
Rhenium	Re	75	186.207
Rhodium	Rh	45	102.9055
Roentgenium	Rg	111	[280]
Rubidium	Rb	37	85.4678
Ruthenium	Ru	44	101.07
Rutherfordium	Rf	104	[267]
Samarium	Sm	62	150.36
Scandium	Sc	21	44.955912
Seaborgium	Sg	106	[271]
Selenium	Se	34	78.96
Silicium	Si	14	28.0855
Silver	Ag	47	107.8682
Sodium	Na	11	22.9897693
Strontium	Sr	38	87.62
Sulphur	S	16	32.065
Tantalum	Ta	73	180.94788
Technetium	Tc	43	[98]
Tellurium	Te	52	127.6
Terbium	Tb	65	158.92535
Thallium	Tl	81	204.3833
Thorium	Th	90	232.03806
Thulium	Tm	69	168.93421
Tin	Sn	50	118.71
Titanium	Ti	22	47.867
Ununbium	Uub	112	[285]
Ununhexium	Uuh	116	[293]
Ununoctium	Uuo	118	[294]
Ununpentium	Uup	115	[288]
Ununquadium	Uuq	114	[289]
Ununtrium	Uut	113	[284]
Uranium	U	92	238.02891
Vanadium	V	23	50.9415
Wolfram	W	74	183.84
Xenon	Xe	54	131.293
Ytterbium	Yb	70	173.054
Yttrium	Y	39	88.90585
Zinc	Zn	30	65.38
Zirconium	Zr	40	91.224

¹ Der Wert in eckigen Klammern, wie z.B. [145], gibt die Atommasse des langlebigsten Isotops des betreffenden Elements an, da das Element keine stabilen Nuklide hat.

(II) Chemical formulas and molar masses of essential compounds related to gypsum

Chemical formula	Molar mass
Al ₂ O ₃	101.961277
BaSO ₄	233.3896
CO ₂	44.0095
CaCO ₃	100.0869
CaC ₂ O ₄ •2H ₂ O	164.12756
CaCl ₂	110.984
CaCl ₂ •6H ₂ O	219.07568
CaF ₂	78.0748064
CaO	56.0774
Ca(OH) ₂	74.09268
Ca(HSO ₃) ₂	202.22028
CaS	72.143
CaSO ₃	120.1412
CaSO ₃ •½H ₂ O	129.14884
CaSO ₄	136.1406
CaSO ₄ •½H ₂ O	145.14824
CaSO ₄ •2H ₂ O	172.17116
CaSiO ₃	116.1617
FeO	71.8444
Fe ₃ O ₄	231.5326
Fe ₂ O ₃	159.6882
Fe(OH) ₃	106.86702
FeSO ₄	151.9076
FeSO ₄ •7H ₂ O	278.01456
H ₂ O	18.01528
½H ₂ O	9.00764
1 ½H ₂ O	27.02292

Chemical formula	Molar mass
Al ₂ O ₃	101.961277
BaSO ₄	233.3896
CO ₂	44.0095
CaCO ₃	100.0869
CaC ₂ O ₄ •2H ₂ O	164.12756
CaCl ₂	110.984
CaCl ₂ •6H ₂ O	219.07568
CaF ₂	78.0748064
CaO	56.0774
Ca(OH) ₂	74.09268
Ca(HSO ₃) ₂	202.22028
CaS	72.143
CaSO ₃	120.1412
CaSO ₃ •½H ₂ O	129.14884
CaSO ₄	136.1406
CaSO ₄ •½H ₂ O	145.14824
CaSO ₄ •2H ₂ O	172.17116
CaSiO ₃	116.1617
FeO	71.8444
Fe ₃ O ₄	231.5326
Fe ₂ O ₃	159.6882
Fe(OH) ₃	106.86702
FeSO ₄	151.9076
FeSO ₄ •7H ₂ O	278.01456
H ₂ O	18.01528
½H ₂ O	9.00764
1 ½H ₂ O	27.02292

(III) Conversion factors for flue gas desulphurization processes**a) Different absorbants**

1 t	CaCO ₃	are obtained from	1.72 t	CaSO ₄ •4H ₂ O
1 t	Ca(OH) ₂	are obtained from	2.32 t	CaSO ₄ •4H ₂ O
1 t	CaO	are obtained from	3.07 t	CaSO ₄ •4H ₂ O

1 t	CaSO ₄ •2H ₂ O	are required for:	0.58 t	CaCO ₃
			0.43 t	Ca(OH) ₂
			0.33 t	CaO

1 t	CaSO ₄ •2H ₂ O	consists of	0.209 t	H ₂ O
			0.326 t	CaO
			0.465 t	SO ₃

		respectively	0.209 t	H ₂ O
			0.186 t	S
			0.233 t	Ca
			0.372 t	O ₂

b) Quantities of gypsum obtained from sulphur and sulphur compounds

1 t	S	are obtained from	5.37 t	CaSO ₄ •2H ₂ O
1 t	SO ₂	are obtained from	2.69 t	CaSO ₄ •2H ₂ O
1 t	SO ₃	are obtained from	2.15 t	CaSO ₄ •2H ₂ O
1 t	CaSO ₃ •½H ₂ O	are obtained from	1.33 t	CaSO ₄ •2H ₂ O
1 t	Ca(HSO ₃) ₂	are obtained from	0.85 t	CaSO ₄ •2H ₂ O

c) Conversion factors for limestone to gypsum - gravimetric and volumetric

1 t	Limestone powder	presumption:	1.3 t/m ³	mean bulk density
1 t	FGD gypsum wet (10 % F)	presumption:	0.9 t/m ³	mean bulk density
1 t	FGD gypsum otro ¹	presumption:	1.0 t/m ³	mean bulk density
1 t	Limestone powder	result in	1.7 t	FGD gypsum otro ¹
1 t	Limestone powder	result in	1.9 t	FGD gypsum wet (10 % F)

The resultant m³-relation is:

1 m ³	Limestone powder	result in	2.77 m ³	FGD gypsum wet (10 % F)
1 m ³	Limestone powder	result in	2.21 m ³	FGD gypsum otro ¹

¹ otro / otro

Abbreviation for "absolute dry". In the paper manufacture an extent for the dryness degree of paper and pulp. The indication is made in "% otro". Base is 0% water content. Because the reading is not yet exactly to determine, it is nowadays replaced by "otro" (oven dry). This is the state of a material after drying under defined conditions.

(IV) Characteristics of the phases in the system $\text{CaSO}_4 / \text{H}_2\text{O}$

Chemical formula of phase	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	$\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	CaSO_4 III	CaSO_4 II	CaSO_4 I
Particularities		2 forms: β form α form	3 limit cases: β - anhydrite III β - anhydrite III' α - anhydrite III	3 reaction stages of calcined anhydrite: A II-s (sparingly sol.) A-II-u (insoluble) A-II-E (estrich plaster)	
Name of phase	hydrated calcium sulfate	hemihydrated calcium sulfate	anhydrite III	anhydrite II	anhydrite I
Other names	Gypsum, raw gypsum. synthetic gypsum, chemical gypsum, industrial gypsum, Waste gypsum, set gypsum	β hemihydrate stucco β gypsum α -hemihydrate autclave α gypsum	soluble anhydrite	anhydrite, raw or natural synthetic or chemical anhydrite, calcinated anhydrite	high-tem- perature an- hydrite
Crystal water (% weight)	20.92	6.21	0.00	0.00	0.00
Density (g/cm^3)	2.31	2.619 – 2.637	2.580	2.93 – 2.97	not determined
Molar mass	172.17	145.15	136.14	136.14	136.14
Hardness (Mohs)	2	–	–	3 – 4	–
Solubility of gypsum in water at 20 °C (g/l)	2.05	8.8	as hemihydrate	2.7	–
Refraction index	n_d n_p n_x	1.559 1.5595 1.584	1.501 1.501 1.546	1.570 1.576 1.614	not determined not determined not determined
Thermodynam stability (°C)	< 40	metastable	metastable	40 – 1180	> 1180
Formation temperature in lab (°C)	< 40	25 – 200 in dry air > 45 in aqueous medium	50 vacuum 100 air 100 dry β -AIII'	200 – 1180	> 1180, not stable below 1180
Formation temperature, field (°C)	< 40	120 – 180	290 β -AIII 290 β -AIII' 110 α -AIII	general: 300 – 900. > 500: AII-s 500 – 700: AII-u > 700: AII-E	–