SULPHUR
18

ISO common name	-
Chemical name	Sulphur (IUPAC); sulfur (CA; *7704-34-9*)
Empirical formula	S_x
Atomic mass	32.06
m.p.	114.5 °C. Allotropic forms, rhombic: 112.8 °C; monoclinic: 119 °C
v.p.	5.3×10^{-4} Pa at 30.4 °C
d_4^{20}	2.07 (rhombic)
n_D	1.957 (rhombic)
Solubility	In water: practically insoluble. The rhombic form is readily soluble in carbondisulphide, whereas the amorphous is not. Slightly soluble in ethanol and diethyl ether
Description	Yellow solid
Stability	Oxidises slowly at normal temperatures
Formulations	Wettable powders, air milled powders, dustable powders and suspension concentrates

SULPHUR TECHNICAL
*18/TC/M/-

1 Sampling. Take at least 100 g.

2 Identity test -

3 Sulphur

SCOPE The method is applicable to all formulations based on sulphur. If thiosulphate or other sulphur compounds are present a correction must be made for them since both free and combined sulphur are determined.

OUTLINE OF METHOD The sulphur is converted by refluxing with sodium sulphite to sodium thiosulphate. The thiosulphate is then titrated with standard iodine solution.

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*CIPAC method 1967. Prepared by the Sulphur Subcommittee of PAC; Chairman, R de B Ashworth. J Henriet made a major contribution of the work of the subcommittee.

REAGENTS

Sodium sulphite crystals; $Na_2SO_3 \times 7 H_2O$
Formaldehyde 35% solution
Ethanol 95%
Acetic acid 20% aqueous solution
Iodine standardized solution, *c* $(1/2 I_2) = 0.1$ mol/l, RE 16.1
Starch indicator solution, RE 27

APPARATUS

Weighing bottle
Conical flasks, 300 ml with ground glass necks
Reflux condenser to fit the end of the condenser should be square cut, not oblique, so that the walls of the flask are washed down by the refluxing mixture (see Fig. 2)
Measuring cylinder, 50 ml
Measuring cylinder, 25 ml
Volumetric flask, 250 ml
Pipette, 100 ml
Burette, 50 ml

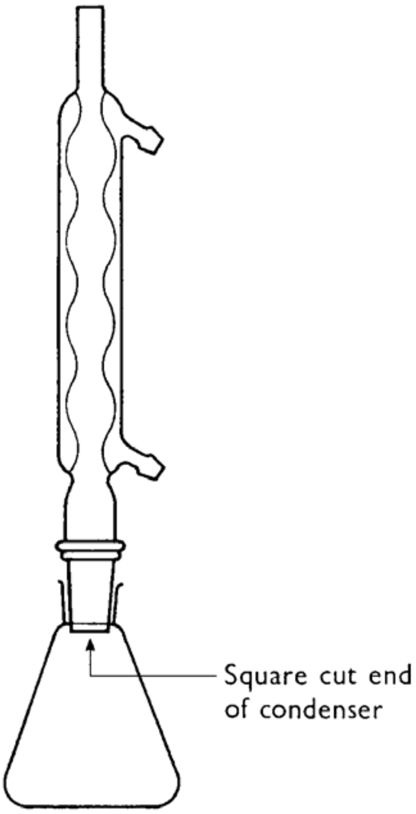

Fig.2 Reflux condenser and flask assembly

PROCEDURE

(a) Determination. Weigh (to the nearest 0.1 mg) sufficient sample (*w* g) to contain about 0.250 g of sulphur, and transfer to a conical flask. Wet the sample thoroughly with ethanol (25 ml). Add water (30 to 40 ml) and sodium sulphite (5 g). Attach the reflux condenser, warm the mixture slowly to dissolve the sulphur, then boil for 1 h shaking the flask from time to time. At the end of this time all the particles of sulphur ought to be dissolved. If not, continue heating the mixture. If elemental sulphur is present shake the flask frequently in order to wash the particles of undissolved sulphur back into the flask. Cool the solution, remove the condenser, and transfer quantitatively, to the volumetric flask. Make up to the mark with water, mix thoroughly, filter if necessary and pipette 100 ml into a conical flask. Add formaldehyde (12.5 ml) and allow the mixture to stand for 5 min. Add acetic acid (10 ml) and titrate immediately with iodine (*t* ml) using starch as indicator.
1 ml iodine, c ($1/2\ I_2$) = 0.1 mol/l ≡ 0.032 g sulphur

(b) Calculation

$$\text{Sulphur content } \frac{8.02 \times t}{w} \text{ g/kg}$$

where:
t = ml required for the sample determination
w = mass of sample taken (g)

(c) Correction for thiosulphate. Weigh (to the nearest 0.1 mg) sufficient sample (*m* g) to contain about 0.250 g of sulphur and transfer to a 250 ml flask. Add water to suspend the product and shake the mixture to dissolve the thiosulphate. Make up to the mark, mix thoroughly, and filter or centrifuge the suspension at 3000 r.p.m. for 15 to 30 min. Pipette 100 ml into a 300 ml titration flask, add formaldehyde (12.5 ml) and allow to stand for 5 min. Add acetic acid (10 ml) and titrate immediately with iodine solution (*b* ml) using starch as indicator.

(d) Correction

$$\text{Sulphur content from thiosulphate present } = \frac{8.02 \times b}{m} \text{ g/kg}$$

where:
b = ml required for the thiosulphate determination
m = mass of sample taken (g)
Subtract the content found from that obtained under *(b)*.

4 Arsenic

OUTLINE OF METHOD The sulphur is oxidized by bromine and nitric acid to sulphuric acid. The arsenic present is reduced to arsine and is determined colorimetrically with silver diethyldithiocarbamate.

REAGENTS

Bromine-carbon tetrachloride reagent. Dissolve two volumes of bromine in three volumes of carbon tetrachloride.
Nitric acid density 1.42. Dilute nitric acid Dilute with distilled water 1 + 2 v/v.
Potassium iodide solution 50% w/v in distilled water
Pyridine analytical reagent grade
Silver diethyldithiocarbamate RE 44. Dissolve 0.5 g in pyridine (100 ml); store away from light. Discard after 2 days.
Tin(II)chloride 2 aq 33% in hydrochloric acid (80 ml of density 1.18), add water (20 ml)
Sulphuric acid density 1.84
Dilute sulphuric acid. Dilute sulphuric acid with distilled water 1 + 3 (v/v)
Hydrochloric acid density 1.18
Zinc shot 16 to 30 mesh
Standard arsenic solutions:
Stock solution. Dissolve arsenic trioxide (1.325 g) in the minimum volume of *c* (NaOH) = 5 mol/l sodium hydroxide (about 4 ml) and dilute to 100 ml with distilled water (1 ml ≡ 10 mg As).
Standard solution. Dilute the stock solution (10 ml) to 100 ml with arsenic free distilled water (1 ml ≡ 1 mg As).
Lead acetate cotton wool. Soak cotton wool in 20% lead acetate solution and dry in warm air.

Note All reagents should be of analytical quality and should be arsenic-free.

APPARATUS

Volumetric flasks 100 ml
Kjeldahl flasks 500 ml
Kjeldahl rack
Test tubes internal diameter 1.3 cm, length 15 cm graduated at 10 ml
Conical flask 100 ml
Ice bath

Gutzeit apparatus See Fig. 4. Fisons Scientific Apparatus Ltd., Loughborough, England, apparatus, modified by sealing 5 cm of glass tube of a suitable diameter to the top of the reagent tube.
Glass scoops
Spectrophotometer

PROCEDURE

(a) Digestion of sample. Weigh (to the nearest 0.01 g) 10 g of the dried sample, into a loosely stoppered Kjeldahl flask in a fume cupboard, and add the bromine-carbon tetrachloride reagent (40 ml). Allow the flask to stand for 30 min with occasional shaking. Add concentrated nitric acid (50 ml) in small portions (do not shake, as a violent reaction may result), swirling the flask to initiate the reaction (it may not begin immediately). Continue the addition of the acid, cooling the flask occasionally in the ice bath to prevent overheating and excessive fumes. If any unoxidized sulphur remains add more bromine-carbon tetrachloride (5 ml) and concentrated nitric acid (10 ml). When all the sulphur is oxidized to sulphuric acid, heat over a moderate bunsen flame to remove bromine, nitric acid and carbon tetrachloride and then, more strongly, until fumes of sulphur trioxide are evolved. If the resulting solution is not colourless, cool, add concentrated nitric acid (10 ml) and repeat the evaporation until fumes of sulphur trioxide are evolved. Cool the solution, add water (50 ml) and evaporate to fumes of sulphur trioxide. Repeat this process three times to remove the last traces of nitric acid. Allow to cool and dilute to the mark in a 250 ml volumetric flask and cool to 10 °C.
(b) Preparation of calibration graph and determination. As for zineb technical **25**/TC/M/5 *(b)*.

SULPHUR AIR MILLED

As for sulphur technical **18**/TC/M/-.

SULPHUR WETTABLE POWDERS

[*]**18**/WP/M/-

1 Sampling Take at least 500 g.

2 Idenity tests -

3 Sulphur As for sulphur technical 18/TC/M/3.

4 Arsenic As for sulphur technical 18/TC/M/4.

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[*] CIPAC method 1967

5 Suspensibility

APPARATUS AND REAGENTS As for MT 15, CIPAC F, *p.* 45, and for sulphur technical **18**/TC/M/3.

PROCEDURE

(a) Preparation of suspension MT 15.1 *(i)*
(b) Determination of sedimentation MT 15.1 *(ii)*
(c) Determination of sulphur in the bottom 25 ml of suspension. Quantitatively transfer 25 ml of suspension, using the minimum amount of water, to a 300 ml conical flask and determine its sulphur content by **18**/TC/M/3. If the presumed sulphur content is greater than 0.25 g take a portion for analysis. Mass of sulphur in 25 ml of suspension = 0.00802 *t* g.

(d) Calculation

$$\text{Suspensibility} = \frac{111(c-Q)}{c}\ \%$$

where:

c = mass of sulphur in the sample taken for the preparation of the suspension (g)
Q = mass of sulphur in the bottom 25 ml of suspension

6 Particle size

OUTLINE OF METHOD A suspension of known concentration of sulphur in water is prepared and poured into the sedimentation tube. For particles of 6 µm or less the amount of sulphur in the top 20 cm of the tube is determined after 166 min. For particles of less than 2 µm the sulphur determination is made after 27 h.

REAGENTS As for **18**/TC/M/3

APPARATUS As for **18**/TC/M/3 together with:
Tapered cylinder, 100 ml, with a cone shaped bottom. A cut-down 100 ml Crow receiver is suitable.
Stout glass rod with a rounded end to fit bottom of receiver
Graduated sedimentation tube (see Fig. 3)

PROCEDURE
Mix the sample thoroughly, weigh (to the nearest mg) about 10 g (*m* g) and transfer to the tapered cylinder. Stir with the stout glass rod with a rounded end (the rod must fit the bottom of the cylinder) and add distilled water very gradually. Continue

to stir the material with water to break up aggregated particles. An uniform technique gives reproducible results. Transfer the mixture quantitatively to a volumetric flask (1 l) and make up to the mark with distilled water, which should be brought to the temperature at which the test is being carried out. Shake the contents of the flask thoroughly and pour the contents into the sedimentation tube up to the 20 cm mark. (In the case of products in which some particles settle very rapidly, determine the capacity of the sedimentation tube to the 20 cm mark; prepare the suspension as before in the open cylinder. Transfer the suspension direct to the sedimentation tube and add distilled water to the 20 cm mark). Allow the sedimentation tube to stand at 22 to 25 °C, avoiding excessive vibration for 166 minutes. Remove the whole of the suspension above the run-off, mix thorougly and determine the sulphur in a 50 ml aliquot of the suspension by **18**/TC/M/3 omitting the ethanol.

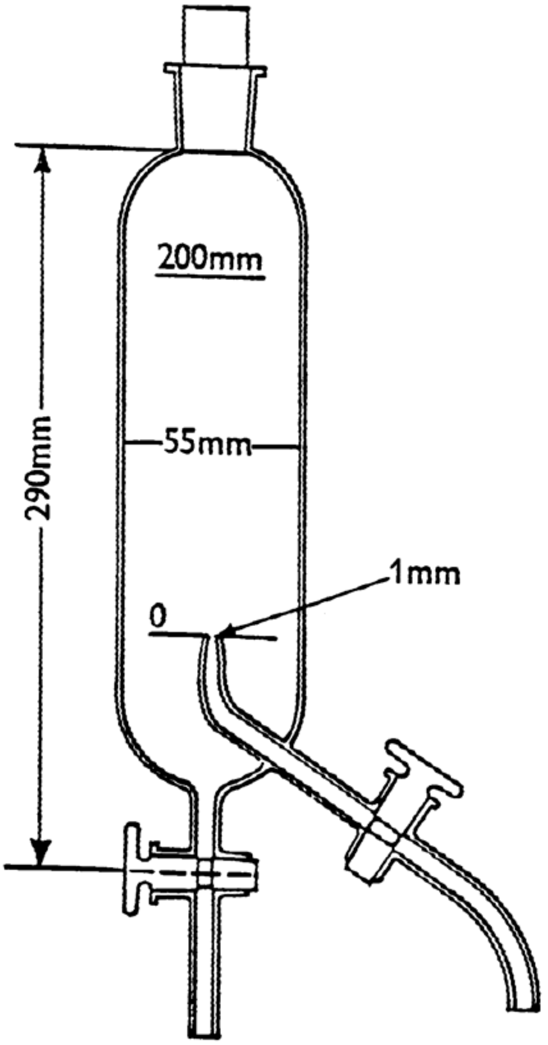

Fig. 3 Graduated sedimentation tube. All dimensions in mm.

$$\text{Sulphur (6 µm or less) in the original sample} = \frac{160000 \times t}{m \times q} \text{ g/kg}$$

where:

q = sulphur content of original sample (g/kg) determined by **18**/TC/M/3
m = mass of sample taken (g)

Repeat the whole procedure, allowing the sedimentation tube to stand for 27 h, determine the sulphur present as before and hence the percentage of particles of 2 µm or less.
The relationship between particle size and time of settling is given by the British Coal Utilization Research Association settling formula, viz.

$$d = 175 \times \sqrt{\frac{\eta}{S - s}} \times \sqrt{\frac{h}{t}}$$

where:

η = viscosity of fluid = 0.01 at 21 °C
S = density of sulphur = 2.07
s = density of water = 1
h = height of settling in cm
t = time (min)
d = diameter of largest particles (µm)
Use MT 42 for air milled powders.

SULPHUR DUSTABLE POWDERS

[*]**18**/DP/M/-

1 Sampling. Take at least 1 kg.

2 Identity tests -

3 Sulphur. As for sulphur technical **18**/TC/M/3.

4 Arsenic. As for sulphur technical 18/TC/M/4.

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[*] CIPAC method 1967

SULPHUR SUSPENSION CONCENTRATES

[*]**18**/SC/M/-

1 Sampling. Take at least 1 kg.

2 Identity tests -

3 Sulphur. As for sulphur technical **18**/TC/M/3.

4 Arsenic. As for sulphur technical 18/TC/M/4.

5 Suspensibility

APPARATUS AND REAGENTS As for MT 161, CIPAC, F, *p*. 394 and sulphur technical **18**/TC/M/3.

PROCEDURE

(a) Preparation of suspension and determination of sedimentation MT 161, CIPAC 1C, *p*. 394.
(b) Determination of sulphur in the bottom 25 ml of suspension. As for sulphur wettable powders **18**/WP/M/5 (c).

6 Particles size. As for sulphur wettable powders **18**/WP/M/6.

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[*] CIPAC method 1967