Determination of total sulphur in inorganic compounds—An overview

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Sulphur is invariably present in all materials either as an impurity or as a major constituent. Several methodologies are available to determine the sulphur content both at trace level and percentage levels. Some of the techniques employed for the determination of total sulphur in inorganic materials have been briefly described in this paper.

Sulphur compounds play an important role in technological and scientific fields. Sulphur can be used as an oxidising or reducing agent depending on the environmental conditions. The largest use of sulphur (about 85% of global production) is in the form of sulphuric acid, which finds applications in almost all industries (fertilizers, chemicals, pigments, steel, rayon and film or petroleum products). In elemental form it is used in paper, pulp and rubber industries. Sulphur can be present as a trace impurity or as a major constituent. It can be present as free or combined form (as sulphide, sulphate or sulphur analogs of carbonyls, carboxylic acids, etc.). Sulphur present even at trace level in stainless steel has a deleterious influence on its mechanical properties (sulphur embrittlement). Though both sulphur and carbon present as an impurity cause damage to the material, not much importance seems to have been given to the determination of sulphur as compared to carbon. This is reflected from the fact that the quantum of work published on estimation of carbon is much higher than that on sulphur; and the commercial equipments for the determination of carbon are many compared to that for sulphur. Sengupta has compared various methods available for the determination of carbon and sulphur in ferrous metals. Most of the recent work is on the determination of sulphur in steel samples. Apart from the determination of total sulphur content, it is essential to find out the sulphur functional group, since the functional group decides the properties of the product. The present overview is limited to the available methods for the determination of total sulphur in solid inorganic materials. The functional group can be determined by employing infrared spectroscopy and mass spectrometry. However, this is beyond the scope of this paper.

Experimental Procedure

Sampling

In the analytical work, sampling of the material is the first and foremost important step. As has been stated by Murphy the only truly representative sample consists of 100% of the material, which is impractical and hence compromise is to be made in choosing the sample size, depending on the accuracy needed. Different techniques have to be followed in sampling depending on (i) on-line collection of samples during the production or (ii) samples to be chosen from bulk materials. In the first case, at regular intervals of production, samples are drawn for the analysis. In the case of gases and homogeneous liquids (after mixing thoroughly) any small portion of the sample is a true representative of the whole lot. In sampling of solids, depending on the nature of the material (tablets/pellets, powder or ingots) an appropriate method is to be chosen. Tablets/pellets are arranged serially and samples are chosen at random. In case of powders, a number of small samples are collected from different parts randomly and mixed. Small portions are collected from this lot and the process is continued till required sample size is achieved. In the case of ingots, holes are drilled in the representative ingots and are mixed, powdered and required amount of sample is collected as mentioned above. Kratochvil and Taylor have given an excellent account on sampling of solid samples for chemical analysis. More details can be obtained from standard quantitative analysis books.
Analysis

Treatment of the sample

After choosing the sample size, the next important step in the analysis is to convert the sulphur to a suitable determinable form. It can be in solid, liquid or gaseous state. Most of the techniques employed for the determination of sulphur are based on the analysis of the sample in liquid form. Hence it is of importance to have knowledge on the various methodologies available to dissolve the sample. Depending on the matrix, suitable medium is chosen. Most of the steel samples go into solution with HNO₃ or HNO₃ + HCl oxidation which converts all forms of sulphur into soluble sulphate. Samples containing silicon are treated with HNO₃ or HCl or HClO₄ in presence of HF. Refractory materials and other inorganic samples containing sulphur, which cannot go into solution by simple acid treatments, are subjected to fusion with mild (sodium/potassium carbonate, magnesium oxide or their mixture) or strong (sodium peroxide, sodium carbonate or potassium chlorate) flux prior to dissolution. Mild fluxes are employed for treating ores and minerals containing small amounts of sulphur. In the fusion, the oxidation of sulphur to sulphate takes place from the atmospheric oxygen. Insoluble barium, calcium, strontium and lead sulphates can be dissolved only after the treatment with fluxes. During the fusion, the insoluble sulphates are converted into soluble sulphate and insoluble metallic carbonates. Yan et al. have used Na₂CO₃ + MgO fusion mixture to dissolve coal. Strong fluxes generally employed are (i) sodium carbonate mixed with KClO₃ or KNO₃ and (ii) sodium peroxide. In the fusion with strong fluxes, the fluxes themselves are capable of oxidizing sulphur without the aid of atmospheric oxygen. Strong fluxes are employed in the dissolution of samples containing higher amounts of sulphur. Sodium peroxide is a powerful oxidising flux which can decompose any type of sample. However, care should be taken that there is no organic material in the sample. Yamada et al. have employed KClO₃ and HNO₃ mixture for the dissolution of metal sulphide. After fusion, the sample is dissolved in water or HCl. An aliquot of the above solution is taken for the determination of total sulphur. In neutron/proton activation analysis sample can be in solid form. In the analytical methods wherein SO₂ or H₂S are monitored, the solid sample is directly oxidised or reduced at high temperatures in presence of oxygen or moist hydrogen. H₂S can also be liberated by reducing the sulphate solution with hydriodic acid and hypophosphorous acid mixture.

Analytical techniques

In the analysis, one should be concerned about the cost, availability of equipment, ease and accuracy of the method. Various methodologies are available for the determination of total sulphur content. They include gravimetry; titrimetry; turbidimetry; spectrophotometry; electro chemical techniques like amperometry, potentiometry, conductometry, polarography, coulometry, voltammetry, sulphur sensors; isotopic techniques, gas chromatography, X-ray emission (fluorescence), combustion cum TC/IR detection, mass spectrometry, ICP-AES and chemiluminescence. Each method has its own advantages and limitations. For the determination of sulphur present in trace levels, turbidimetry, spectrophotometry, mass spectrometry and isotopic techniques can be employed. However to improve the precision, low concentration samples can be pre-concentrated, prior to the analysis. For high sulphur content samples, virtually any method can be adopted by suitable dilution.

Gravimetry

The time tested gravimetric analysis involves the precipitation of sulphate ions as barium sulphate, by the addition of barium chloride. The precipitate is filtered through ashless quantitative filter paper, washed and ignited at 850°C and sulphur is weighed as barium sulphate. Gravimetry is generally employed in samples containing sulphur in bulk.

Titrimetry

In the direct titration method, sulphate ion is titrated with barium perchlorate using thorin as indicator. The end point is sharp and the change in the colour is from yellow to pink. The method is applicable to solutions that do not contain large amounts of foreign ions. Otherwise they have to be purified before titration. An aliquot of the solution is taken in 80% alcohol medium and pH is adjusted to 2-4 with dilute perchloric acid prior to titration. A precision of 10% has been reported at a few mg of sulphur content.

The titration of sulphate employing barium chloride with tetra hydroxyquinone as an indicator is not as sharp as the above method.

In iodimetric titrations, sulphur present in the sample is oxidised to SO₂ by high temperature combustion. The liberated sulphur dioxide is fed to a mixture of standard potassium iodide, hydrochloric acid,
starch solution and small amount of standard potassium iodate. This mixture produces free iodine and the colour of the solution will be blue. \( \text{SO}_2 \) will react with this \( \text{I}_2 \) and \( \text{KI} \) will be formed rendering the solution colourless. This colourless solution is titrated with standard \( \text{KIO}_3 \) while at the same time continuing feeding of the \( \text{SO}_2 \). \( \text{I}_2 \) liberated is instantaneously utilised by \( \text{SO}_2 \) being fed rendering the solution colourless. This process is continued until no more \( \text{SO}_2 \) is available for the neutralisation of the \( \text{I}_2 \) liberated, which is indicated by the persistence of blue colour. From this the sulphur content is calculated. 5 ppmw of sulphur could be determined by this technique.

Sulphate is precipitated as barium sulphate and is dissolved in known excess of EDTA solution in presence of ammonia. Excess amount of EDTA is titrated with standard magnesium salt using erichrome black \( T \). The amount of EDTA consumed for the dissolution is proportional to the sulphur content. Guudzhev determined 0.04-0.4% of sulphur at 2.2% R.S.D. Fontan and Olsina have developed an indirect method using \( \text{Cu(II)} \)-3,5 PADAB indicator for the determination of sulphur in iron and other oxides.

In another method, sulphur in the sample is reduced to \( \text{H}_2\text{S} \) at 850-900°C in presence of hydrogen, HI and \( \text{NaH}_2\text{PO}_2 \). The liberated \( \text{H}_2\text{S} \) is absorbed in alkaline solution and titrated against standard \( \text{Hg(OAc)}_2 \) solution in presence of dithiozone indicator.

**Turbidimetry and nephelometry**

These techniques are applicable for colourless solutions and for very low concentrations of sulphate. A suspension is formed by employing glycol-ethanol-water mixtures. The absorption (turbidimetry) or scattering (nephelometry) of light is applied on the suspension. 5 \( \mu \text{g} \) of sulphur at ±1% precision has been determined by this method. In another method, the turbidity formed by \( \text{BaCl}_2 \) has been employed for the measurement. These are proportional to sulphur concentrations. Yan et al. have analysed coal samples with RSD 0.44% with a recovery of 99.2-100.9%. Siriwardena has determined sulphur up to 2ppmw in cyanide extracts of gold and plating solutions after converting all forms of sulphur to sulphate by \( \text{H}_2\text{O}_2 \) treatment.

**Spectrophotometry**

Sulphur containing sample is dissolved in a suitable medium. Sulphur is then reduced to \( \text{H}_2\text{S} \) employing hydriodic and hypophosphorous acid mixture. It is then converted into Lauth’s violet employing \( p \)-phenylenediamine in presence of an oxidising agent such as ferric ion and the absorbance is measured spectrophotometrically at 595 nm. In another method, \( \text{H}_2\text{S} \) formed by the reduction of stainless steel was absorbed in alkali and absorbance at 232 nm is monitored. From the calibration plot of absorption versus concentrations, the sulphur content in the sample is obtained. Acs and Barabas have oxidised sulphur to sulphur dioxide and determined it by spectrophotometrically with pararosaniline and formaldehyde and could estimate 5ppmw of sulphur. Abdel and El Shahat have determined sulphur in various types of samples using ferricyanide-thymolpthaleine reagent and measuring absorbance at 592 nm. Lai et al. have absorbed the liberated \( \text{SO}_2 \) during combustion in standard \( \text{KMnO}_4 \) solution and measured absorbance at 530 nm. They observed that Beer’s law is obeyed up to ±0.04% sulphur.

**Electro chemical methods**

**Amperometry**

Sulphate in the solution can be directly titrated using standard lead nitrate solution to an amperometric end point in alcohol medium. Alternatively, in an indirect method, sulphate is precipitated as lead sulphate, which is dissolved, and the lead content is determined by titrating with standard dichromate solution. From the amount of titrant consumed, the sulphur content can be calculated. Sheu et al. have determined sulphur in \( \text{CuInS}_2 \) at 10 mg sample size with +0.16% error and RSD ± 0.17%, employing amperometry.

**Potentiometry**

Garcia-Calzada et al. have employed potentiometric analysis using sulphide selective electrode, for low sulphur content samples. The sulphur in solid sample is reduced to \( \text{H}_2\text{S} \) employing HI and \( \text{H}_3\text{PO}_2 \) mixture. \( \text{H}_2\text{S} \) gas formed is absorbed in sodium hydroxide solution containing ascorbic acid or hydrazine. It is then titrated using sulphide selective electrode. The method is used to solutions containing \( 10^3 \) M sulphur with a precision of ±5%. Bebesko and Oleshko have used a mixture of phosphoric acid, tin chloride and trivalent titanium to reduce sulphur in the sample to \( \text{H}_2\text{S} \) and estimated it by sulphide selective electrode.

**Conductometry**

The electrical conductivity of the sulphate solution
is measured after successive additions of standard barium chloride/nitrate/acetate solution. The amount of titrant at the point of change in slope of electrical conductivity is proportional to the concentration of sulphur. In another method, SO₂ formed by the combustion of sulphur present in the sample is absorbed in H₂O₂ and the electrical conductivity of the resulting H₂SO₄ has been measured which is proportional to the sulphur content. Employing this technique, a precision of ±10% was achieved at 1500 ppmw level.

**Polarography**

Sulphur is reduced to H₂S and the gas is absorbed in suitable electrolyte like sodium hydroxide or sodium hydrogen phosphate. Sulphide ion polarises the dropping mercury electrode resulting in anodic wave. The height of the anodic wave (diffusion current) is proportional to the sulphur content. Ravenda could determine H₂S over the range 5×10⁻⁴ - 3×10⁻³ M. Han et al. have absorbed H₂S liberated during the hydrogen reduction of sulphur in cadmium acetate solution and determined sulphur using dropping mercury electrode. The ease with which various sulphides get reduced at 800°C in presence of hydrogen has also been incorporated in their studies.

**Coulometry**

Sulphur is oxidised to SO₂ and is absorbed in acidified bromide solution and the liberated bromine is titrated electrolytically. From this sulphur content can be obtained. Lemm et al. determined SO₂ liberated by the combustion of the sample in oxygen and argon mixture by coulometry over the range 1-1000 ppmw. Song has studied the analysis of sulphur in coal by applying iodimetry - coulometric titration and could achieve a standard deviation of ±0.03%. Jiang et al. have converted SO₂ formed during the combustion of iron ore into H₂SO₄ by the electrolytic action. This has been titrated by coulometry and over a wide range. Persits et al. have roasted the sulphur containing sample in dry oxygen at 1250 - 1300°C and after absorption of SO₂ formed in aqueous electrolyte solution and carried out coulometric titration. Will's et al. could determine sulphur from a sample size of 0.5-20 mg containing 0.5-100% sulphur. The methodology includes trapping of all the oxides of sulphur liberated during the combustion of sample in hydrogen peroxide, volatalising the trap contents and sweeping with nitrogen gas through hot copper maintained at 890°C, to convert all sulphur oxides quantitatively into SO₂, followed by coulometric titration with iodide.

**Voltammetry**

Yamada et al. have developed anodic stripping voltammetry (ASV). The method involves dissolving samples and precipitation of sulphate ions as lead sulphate by the addition of excess of standard lead nitrate solution. Unreacted lead is determined by ASV employing mercury coated platinum micro electrode. In a sample size of 10-15 mg, a standard deviation of ±0.004% has been reported.

**Solid state sensors**

Recently Zhang et al. have developed solid state electrochemical sulphur sensors for the determination of sulphur in molten metals. The sensors have fast response time with good precision. Various methods involved in the preparation of these sensors have been discussed. Gozzi and Granati have employed solid-state electrochemical sensor for in situ monitoring of sulphur in carbon-saturated iron.

**Isotopic techniques**

There are two different techniques employed for sulphur determination in the samples viz: (i) activation analysis and (ii) tracer method.

**Neutron activation analysis**

³⁵S is β active and has half-life of 87 days, and may be produced by neutron irradiation of ³⁴S, which has abundance of 4.2%. Similarly ³²S (95% abundance) with (n,p) reaction gives β active ³²P which has 14 days half-life. In activation analysis either of these two β active isotopes is monitored. In the absolute method, the sample is irradiated, purified and β activity is measured. Das and Bhattacharyya have determined sulphur (0.25-3%) by monitoring 1.72MeV photo peak belonging to ³²P produced from ³²S(n,p)³³P reaction. In another method Klie and Sharma have monitored intensity of 2130 KeV γ photo peak belonging to ³³P produced by ³³S (n,p)³³P reaction. From this the sulphur content can be calculated. In standard comparison method a standard with known sulphur content and sample are irradiated simultaneously and from the ratios of ³³S or ³³P formed, the sulphur content is calculated. Soutis could determine 20 ppmw of sulphur by standard comparison method with an error of less than 5%.

**Proton activation analysis**

Proton activation analysis employing 10.3 Mev
### Table 1—Various techniques for the determination of sulphur

<table>
<thead>
<tr>
<th>Technique</th>
<th>Methodology</th>
<th>Nature of sample</th>
<th>Quantity of S and precision</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravimetry</td>
<td>Weighed as BaSO₄</td>
<td>Any</td>
<td>For bulk S content</td>
<td></td>
</tr>
<tr>
<td>Titrimetry</td>
<td>Titration of sulphate ion with barium perchlorate using thorin as indicator</td>
<td>Water samples</td>
<td>10 ± 1 ppm Higher content: &lt;1% error</td>
<td>10,11</td>
</tr>
<tr>
<td></td>
<td>With barium chloride using tetrahydroxy quinone as indicator</td>
<td></td>
<td></td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>Iodometry</td>
<td>Se-S mixtures</td>
<td>5 ppm</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>EDTA titration using Erichrome Black-T as indicator</td>
<td>Cast iron and other oxides</td>
<td>0.04 - 0.4% with &lt; 2.2% RSD</td>
<td>14,15</td>
</tr>
<tr>
<td></td>
<td>Erichrome Black-T and Methyl red indicator</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>H₂S liberated from sample titrated with Hg₂(OAc)₂ with dithiozone indicator</td>
<td>Inorganic salts, org. compounds and drugs</td>
<td>820 ppm with RSD ± 1%</td>
<td>16</td>
</tr>
<tr>
<td>Turbidity and Nephelometry</td>
<td>Turbidity formed by BaCl₂</td>
<td>Organic substances</td>
<td>to 100 ppm with ± 1% RSD</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Plant materials</td>
<td>3-4% RSD</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coal samples</td>
<td>1-5 mg SO₂/50 ml with RSD</td>
<td>7</td>
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<tr>
<td></td>
<td></td>
<td>Cynide extraction of gold ore and plating materials</td>
<td>0.44% RSD</td>
<td>20</td>
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<tr>
<td>Spectro-Photometry</td>
<td>Reduce S to H₂S and develop colour with p-phenylenediamine</td>
<td>Ceramic materials</td>
<td>10 - 600 ppm with 12% &amp; 3% RSD at lower and higher amounts</td>
<td>9</td>
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<tr>
<td></td>
<td></td>
<td>SS samples</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>Oxidise S to SO₂ and colour development using pararosaniline and formal dehyde</td>
<td>Selenium</td>
<td>5-1200 ppm with ± 2% RSD</td>
<td>22</td>
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<tr>
<td></td>
<td>Oxidise S to SO₂ and colour development using ferricyanide and thymolphthaleine</td>
<td>In mixtures of S compounds</td>
<td>Error ± 0.2%</td>
<td>23</td>
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<tr>
<td></td>
<td>Oxidise S to SO₂, absorb in KMnO₄ and measure at 530 nm</td>
<td>Steel samples</td>
<td>0.002 - 0.04 % S</td>
<td>24</td>
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<td>Amperometry: titrate sulphate ion with Pb(NO₃)₂</td>
<td>CuInS₂</td>
<td>0.01-0.001 M</td>
<td>25</td>
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<td></td>
<td>Sulphate ion precipitated as lead sulphate, dissolved and lead titrated with dichromate</td>
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<td>with 0.17 % RSD</td>
<td>27</td>
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<td></td>
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<td>CaS and K₂SO₄</td>
<td>200 - 700 ppm with RSD ± 5%</td>
<td>28</td>
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<td></td>
<td>Conductometry: sulphate ion titrated with barium ion</td>
<td></td>
<td></td>
<td>29</td>
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<td></td>
<td>SO₂ liberated by oxidation absorbed in H₂O₂ and conductivity of resulted H₂SO₄ measured</td>
<td>Coal tar fractions</td>
<td>20 - 4000 ppm with 0.7% RSD at 1500 ppm</td>
<td>30</td>
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(Contd)
<table>
<thead>
<tr>
<th>Technique</th>
<th>Methodology</th>
<th>Nature of sample</th>
<th>Quantity of S and precision</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polarography:</td>
<td>Reduce sulphur to ( \text{H}_2\text{S} ), absorb in suitable electrolyte.</td>
<td>Sulphides of Mg, Ca, Ba and Rare earths</td>
<td>(5 \times 10^{-2} - 3 \times 10^{-3} ) M</td>
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<td></td>
<td>Height of anodic wave proportional to sulphur content</td>
<td></td>
<td></td>
<td>33</td>
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<tr>
<td>Coulometry:</td>
<td>Sulphur oxidised to ( \text{SO}_2 ), absorbed in suitable medium and titrated electrolytically</td>
<td>Iron and unalloyed steels</td>
<td>0.8 - 1064 ppm</td>
<td>35, 39</td>
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<tr>
<td></td>
<td></td>
<td>Coke</td>
<td>Std.Dev. ± 0.03%</td>
<td>36</td>
</tr>
<tr>
<td>Voltammetry:</td>
<td>Precipitate sulphate ion with excess ( \text{Pb(NO}_3))_2, and determine unreacted Pb by ASV Solid state sensors</td>
<td>Molten metals</td>
<td>13 - 140 ppm</td>
<td>40, 41, 42</td>
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<td>Isotopic techniques</td>
<td>Neutron activation:</td>
<td>Coal</td>
<td>0.25 - 3%</td>
<td>43, 44</td>
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<tr>
<td></td>
<td>Paper and beer</td>
<td></td>
<td>20 ppm with error &lt; 5%</td>
<td>45</td>
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<td></td>
<td>Proton activation:</td>
<td>Coal</td>
<td>1500 ppm with RSD 2%</td>
<td>46</td>
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<td></td>
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<td>NIST thin films</td>
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<td>47</td>
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<td>49</td>
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<td>XRF</td>
<td>Environmental solids Zinc ore Lighter elements</td>
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<tr>
<td>Combustion TC/IR detection</td>
<td>Oxidised Sulphur to ( \text{SO}_2 ), purified and detected by TC or IR detector</td>
<td>Metals, alloys, ores, steel, ceramic materials</td>
<td>ppm to % level with 2 - 10% RSD</td>
<td>53 - 62</td>
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<tr>
<td>Mass spectrometry</td>
<td>Oxidised Sulphur to ( \text{SO}_2 ) and measure pressure and composition</td>
<td>Ceramic materials, sulphides Copper Solids, liquids and gases</td>
<td>ppm to % level with 3 - 10% RSD</td>
<td>63</td>
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<td></td>
<td>Vacuum fusion, mass spectrometry Flash combustion followed by GCMS TIMS</td>
<td>Cu and Fe alloys Pb and Ba sulphides Steel samples</td>
<td>3 - 80 ppm with RSD 0.16%</td>
<td>66</td>
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<td></td>
<td>TIMS, for isotopic compositions IDMS</td>
<td>NIST and SS samples</td>
<td>60 - 3300 ppm with 1% RSD</td>
<td>68</td>
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<tr>
<td>ICP-AES</td>
<td>Reduced to ( \text{H}_2\text{S} ), fed to ICP-AES</td>
<td>Semiconductors</td>
<td>0.5 ppm</td>
<td>70</td>
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<tr>
<td>Chemiluminescence</td>
<td>Reduced to ( \text{H}_2\text{S} ), fed to hydrogen flame and chemiluminescence measured</td>
<td>Cast steel and low alloy steel</td>
<td>0.5 ppm with precision 3%</td>
<td>71</td>
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</tbody>
</table>
protons [\(^{34}\text{S} \text{(p,n)}^{34}\text{Cl}\)] has also been developed\(^{46}\). However minimum 1500 ppmw could be determined.

The nuclear reaction \(^{32}\text{S(d,p)}^{33}\text{S}\) gives 7 peaks well visible on the energy spectra of the emitted protons over the range 1100 and 1450 keV. Based on this David et al.\(^{47}\) have analysed nickel sulphide thin films for sulphur content.

**Tracer technique**

This method is based on the principle that the chemical behavior of all isotopes is same and in direct contact of sample with \(^{35}\text{S}\) tracer results in equilibrium of \(^{35}\text{S}\) between the sample and the tracer through exchange reactions. The exchange between the tracer and the sample is allowed to take place by chemical reactions, separations, solubilites and or coprecipitation. From the isotopic composition of tracer before and after equilibration, the sulphur content in the sample is calculated. By using this technique 10\(^{-18}\) g of sulphur can be determined. Kohl et al.\(^{48}\) have discussed the amount of tracer required for various types of jobs.

**Gas chromatography**

Sulphur in the sample is oxidised to \(\text{SO}_2\) or reduced to \(\text{H}_2\text{S}\) and the gas is analysed by gas chromatography. From the pressure and composition data sulphur content is calculated. By employing silica gel column, 100 ppmw of sulphur in ferrous materials was determined after combustion to \(\text{SO}_2\)\(^{49}\).

**X-ray emission (fluorescence)**

In this technique, the sample is irradiated with high intensity X rays. The changes in the energy appear as photons with characteristic wave lengths of the atom. The frequency of occurrence of these fluorescent X-rays is a measure of the concentration of the element present. Meduna and Schaefer\(^{50}\) have determined sulphur in environmental samples while Gyves et al.\(^{51}\) have determined sulphur in zinc ore. The analytical range of lighter elements was extended by excitation with tungsten L\(_{\alpha}\) radiation\(^{52}\).

**Combustion cum TC/IR detection**

Sample is subjected to combustion in flowing oxygen atmosphere at 1000\(^\circ\)C, and the gases released are purified using various chemical traps. Purified \(\text{SO}_2\) is detected by thermal conductivity detector\(^{53}\) or infrared detector\(^{54}\). Chinese and Japanese\(^{55-62}\) have carried out extensive work on the analysis of sulphur in steels, by combustion followed by infrared detection. The technique is quite fast and 5ppmw of sulphur can be estimated.

**Mass spectrometry**

The sample is subjected to combustion in limited supply of oxygen or oxygen generator at low pressures. Gases evolved are pumped into a known volume. The pressure and gas composition are measured using differential oil manometer and a quadrupole mass spectrometer. From the data sulphur content is calculated\(^{63}\). The method, though time consuming, is absolute one and can be applied for trace level to percentage level of sulphur. The overall precision of 10\% at trace levels and 3\% at bulk ranges was achieved. Hickam\(^{64}\) measured 1-50 ppmw of sulphur by combination of vacuum fusion-mass spectrometry. Baccanti and Colombo\(^{65}\) have determined sulphur by carrying out flash combustion at 1800\(^\circ\)C and estimation of sulphur as \(\text{SO}_2\) by gas chromatographic separation followed by mass spectrometric determination (GCMS). Employing this technique, isotopic ratios and sulphur content in solids, liquids and gases were determined. Paulsen and Kelly\(^{66}\) have determined sulphur as \(\text{AsS}_2\) while Ramakumar et al.\(^{67}\) have monitored metal\(^{8}\) for the determination of isotopic ratios of sulphur by TIMS. Watanabe\(^{68}\) and Kelly et al.\(^{69}\) have determined sulphur in steel samples by isotopic dilution mass spectrometry (IDMS) using \(^{34}\text{S}\) as spike.

**ICP-AES**

Okada et al.\(^{70}\) have determined sulphur in samples containing 0.5 ppmw S. The methodology involves oxidizing the sample in presence of phosphoric acid and an oxidising agent followed by reduction of sulphur to \(\text{H}_2\text{S}\) in presence of reducing agent at 200 - 400\(^\circ\)C. This \(\text{H}_2\text{S}\) is introduced in ICP and excited emission intensity is measured, which is proportional to the concentration of sulphur. Garcia et al.\(^{71}\) have employed ICP-AES on \(\text{H}_2\text{S}\) generated by reduction of the sample with a detection limit of 20 ppb sulphur and established ± 3\% precision at 0.5 ppmw level.

**Chemiluminescence**

Kuss\(^{72}\) has reduced sulphur to \(\text{H}_2\text{S}\) by HI, HCl and \(\text{NaH}_2\text{PO}_4\) at 135\(^\circ\)C. \(\text{H}_2\text{S}\) is then swept by an auxiliary gas, argon or nitrogen into a hydrogen diffusion flame wherein \(\text{H}_2\text{S}\) converts into sulphur molecules. The chemiluminescence of this reaction is measured at 350-410 nm.
Conclusions

In the present overview, most of the available methods for the determination of total sulphur have been described. The methodologies, nature of the sample analysed and the amount of sulphur estimated with the precision quoted by various researchers is given in the form of a table. The fastest and most commonly used method is combustion cum infrared detection technique. It is known that there exists an equilibrium between SO₂ and SO₃ formed and the equilibrium shifts towards SO₂ with increase in temperature. Unless high temperatures are applied for combustion (> 1400°C), trace amounts of SO₃ may be formed, which could be left undetected. Hence, it is necessary to generate calibration graphs using standards with same matrix. However, availability of such standards is limited.

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