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REVIEWS

Methods for Assessing the Impurity Composition of High-Purity Sulfur

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Abstract—The review primarily considers the scientific progress in the identification of impurities, molecular compounds, and heterophase inclusions in high-purity sulfur. Methods for their determination, established by the present time, based on atomic emission spectrometry, mass spectrometry, colorimetry, gravimetry, titrimetry, turbidimetry, conductometry, gas chromatography, infrared spectrometry, chromatography–mass spectrometry, and laser ultramicroscopy are thoroughly characterized.

Keywords: high-purity sulfur, impurities, limit of detection, analytical methods

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High-purity sulfur is in demand across various fields of science and technology. It is used for the production of chalcogenide glasses, highly transparent in the mid-IR region [1–3]. In microelectronics, sulfur is used to synthesize metal sulfides, necessary for manufacturing radiation detectors operating in optical and X-ray spectra, as well as fluorescent screens [2, 4]. Zinc sulfide derived from high-purity sulfur serves as a primary material for fabricating laser components operating in the near and mid-IR regions, including windows, lenses, mirrors, protective shields, and components for aviation and space apparatuses, as well as guidance systems [5]. High-purity sulfur is also used to synthesize cadmium and gallium sulfides, utilized in the production of optical instruments and phosphors [6]. An emerging scientific frontier in optoelectronics involves the utilization of ZnS semiconductor crystals based on isotopically enriched sulfur [7, 8].

The functional properties of materials obtained from high-purity sulfur are significantly affected by the impurities present within it. These impurities can enter the final products and degrade their quality. Such impurities include sulfides, sulfates, oxides, and carbonates of various elements, as well as substances in the molecular form and heterophase inclusions [1, 2, 9–11].

The concentration of many impurities is regulated and determined by the application scope of high-purity sulfur. For example, the concentrations of copper and nickel in zinc sulfide phosphors should not exceed 10^{-6}–10^{-5} wt % [12]. Impurities such as hydrogen, oxygen, and carbon, originating from sulfur, deteriorate the transparency of chalcogenide glasses in the mid-IR region, starting from concentrations of 10^{-8}–10^{-7} wt % [2, 13–15]. Impurities in the form of submicrometer-sized heterophase inclusions significantly affect the energy threshold of bulk destruction in chalcogenide glasses under the action of pulsed laser radiation [16].

The progress in fiber optics, power optics, and semiconductor physics necessitates an increase in the purity of sulfur. Currently, the highest demands for the impurity content are imposed by infrared fiber optics based on arsenic sulfide glasses of the As–S system [17]. Multimode optical fibers made of these glasses exhibit minimal optical loss in the mid-IR region at levels of 12–14 dB/km [18]. To achieve this, the integrated concentration of metal and silicon impurities in sulfur used for the synthesis of these glasses must be decreased to a level below 10^{-5} wt % [19].

Concentrations of individual impurities in the most purified sulfur samples obtained to date range from 10^{-8} to 10^{-4} at %, while their cumulative concentration is at a level of $(1–3) \times 10^{-4}$ at % [20]. Such purity levels are not always sufficient to meet the requirements of advanced and prospective scientific developments. Moreover, the reliable identification and determination of impurities at low concentration levels have recently become increasingly important in the technology of the preparation of high-purity sulfur. This is associated with a growing trend towards the use of nonconventional and secondary sources for its production [1]. The impurity composition of such sulfur may significantly differ from that characteristic of sulfur obtained by the conventional methods and requires thorough investigation. Hence, the development of methods of sulfur analysis aimed at expanding information about the impurities and determining them with lower limits of detection has become a relevant scientific direction.

Methods and capabilities for determining impurities of elements, molecular compounds, and heterophase inclusions in sulfur were described in [1, 2, 10, 21]. Of these, atomic emission spectrometry, mass spectrometry, colorimetry, gravimetry, titrimetry, turbidimetry, conductometry, gas chromatography, infrared spectrometry, chromatography–mass spectrometry, and laser ultramicroscopy have found the widest application for this purpose. Examining their capabilities and utilizing them together for studying impurities in sulfur contributes to a more comprehensive characterization, necessary for optimizing technologies for its deep purification.

This review considers the currently known capabilities of methods for determining impurities of elements, molecular compounds, and heterophase inclusions in sulfur.

IMPURITY COMPOSITION OF SULFUR

The impurity composition of sulfur depends on the composition of sulfur-containing raw materials and methods of their processing. The production involves a multistage process [22–25]. At each technological stage, components of the raw materials, substances used as reagents for its extraction, and products of their interaction with equipment materials and the environment can enter sulfur. A combination of these factors determines the impurity composition of sulfur [2].

In industry, elemental sulfur is obtained from native and sulfide ores, as well as from natural and industrial gases containing sulfur dioxide, hydrogen sulfide, and other sulfur compounds [9, 22–25]. Sulfur is extracted from ores using underground smelting methods. The main impurities in sulfur are accompanying analog elements, such as arsenic, with concentrations ranging from 10^{-3} to 0.1 wt %, as well as carbon, oxygen, and hydrogen in compounds with concentrations up to 0.01–0.1 wt %. Elements present in the host rocks at a sulfur deposit site, such as Ca, Si, Al, Mg, and Fe, are also found in sulfur with concentrations ranging from 10^{-4} to 10^{-2} wt %. During aboveground ore processing, sulfur is extracted by smelting in furnaces or by extraction, often following preliminary flotation enrichment. Aqueous solutions of sulfides, hydrocarbons, and their derivatives are commonly used as extractants. Kerosene, higher alcohols, and oils are utilized as flotation agents [22, 23]. When sulfide ores are roasted, sulfur is primarily converted into dioxide, carbon oxysulfide, and carbon disulfide. These compounds are then regenerated into elemental sulfur.

Catalysts such as bauxite, silica, some metal oxides and sulfites are used in sulfur extraction processes [22, 23, 25]. A characteristic feature of such sulfur is the presence of significant amounts of starting and end products of reactions (sulfur and carbon oxides, carbon disulfide and oxysulfide, water, and catalyst particles). Currently, Russian manufacturers of high-purity sulfur regulate impurity content according to TU 6-09-2546-77 [21] (Table 1).

The physical and chemical properties of sulfur of various grades are regulated by the existing standards [26–28]. Only a relatively small number of impurities are regulated in sulfur (Table 1). There is no information about specific organic substances present, and present-day elemental analysis can control a larger number of impurities in concentrations 2–3 orders of magnitude lower than those presented. Certification data for sulfur also do not give information about the impurities of heterogeneous inclusions. This information is crucial for the development of the physical and chemical foundations and technology for the production of high-purity sulfur.

DETERMINATION OF ELEMENTAL IMPURITIES

Numerous methods can be employed for the elemental analysis of sulfur, including chemical, physical, and physicochemical approaches [2, 20, 21, 29–31]. The most commonly used techniques include arc atomic emission spectrometry, photometry of solutions, typically involving the extraction of an analyte, atomic absorption spectrometry, and, less frequently, X-ray fluorescence spectrometry, and electrochemical and nuclear physics methods. The well-known sulfur analysis procedures vary in sensitivity and are adapted differently to samples of varying purity levels. In analyzing pure sulfur, combined procedures are typically employed, involving impurity preconcentration [29, 32]. In the chemical analytical control of industrial sulfur samples (technical sulfur, sulfur of special purity), elemental analysis tasks usually focus on the determination of metal impurities (Al, Fe, Cd, Co, Ga, Mn, Cu, As, Ni, Sn, Pb, Ag, Te, In, and Mo), and also of Se, Te, As, and P [21, 30].

The total metal impurity concentration in industrial sulfur samples can vary widely (from 10^{-5} to 10^{-2} wt %) depending on the grade. Arc atomic emission spectrometry (AAES) is a convenient, highly available, and reliable method for determining metal impurities and several nonmetal impurities in sulfur at levels of 10^{-6} wt % and above. For the analysis of technical and high-purity sulfur, procedures for the direct determination of impurities and their preconcentration have been developed. In analyzing high-purity sulfur, the concentration of a wide range of metal impurities (such as Al, Ga, Fe, Co, Mn, Cu, As, Ni, Cd, Sn, and Pb) is achieved by removing the matrix through evaporation or oxidation (combustion), as sulfur and its oxides are more volatile than oxides, sulfides, sulfates, and carbonates of many metals.

In determining impurities of Te, In, and Mo, the matrix is converted into sulfuric acid by the action of

Table 1. Concentrations of impurities in high-purity sulfur according to TU 6-09-2546-77 [21]

Impurities	Norm (no more than), wt %		
	high-purity 16-5	high-purity 14-4	high-purity 15-3
Se	2×10^{-4}	Not rated	5×10^{-4}
P	1×10^{-5}	5×10^{-5}	1×10^{-3}
Cl, Br, I (in terms of Cl)	2×10^{-5}	$5 \times 1\,0^{-5}$	1×10^{-4}
Bitumen	2×10^{-3}	2×10^{-3}	2×10^{-3}
Al	4×10^{-5}	1×10^{-4}	1×10^{-4}
Fe	2×10^{-5}	3×10^{-5}	1×10^{-4}
Cd, Mo	1×10^{-6}	Not rated	Not rated
Co	2×10^{-6}	3×10^{-6}	1×10^{-5}
Ga, In	1×10^{-6}	1×10^{-6}	5×10^{-5}
Mn	1×10^{-6}	5×10^{-6}	1×10^{-4}
Cu, Ag	1×10^{-6}	5×10^{-6}	5×10^{-5}
As	2×10^{-5}	3×10^{-5}	5×10^{-4}
Ni, Pb	2×10^{-6}	1×10^{-5}	1×10^{-4}
Sn	1×10^{-6}	1×10^{-5}	1×10^{-4}
Te	5×10^{-6}	Not rated	Not rated

concentrated nitric acid, and the sulfuric acid is subsequently evaporated [21]. A mixture of SiO_2 and NaCl, as well as spectrally pure carbon powder, are used as impurity collectors [21, 33, 34]. The residue after sulfur combustion can be dissolved for the subsequent spectral determination of impurities [35]. The method of matrix removal is usually selected based on the requirements for the extraction coefficient of specific impurities to the concentrate. An undeniable advantage of atomic emission spectrometry is the determination of a wide range of impurities from a single test sample with relatively high sensitivity. Procedures involving impurity preconcentration by matrix removal can be coupled with subsequent determination in a solution of the concentrate using widely used atomic emission or mass spectrometric methods with inductively coupled plasma (ICP–AES, ICP–MS). For example, ICP–AES has been used in conjunction with AAES for determining impurities of Al, As, Ce, Cr, Cu, Fe, Mg, Mn, Ni, Se, Si, Te, Ti, and Zn in sulfur samples of various purities [7].

Impurity preconcentration was achieved by evaporating the matrix with the subsequent conversion of the concentrate into a solution, followed by determination using AAES and ICP–AES. Additionally, the ICP–AES determination of impurities in solutions obtained by the autoclave digestion of sulfur in 68% nitric acid was conducted. The combined use of AAES and ICP–AES allowed for the additional verification of the accuracy of the results. The autoclave digestion of sulfur readily occurs in nitric acid of azeotropic composition (68–69 wt %), which can be obtained in a highly pure form by distillation without boiling, unlike concentrated nitric acid is used for sulfur oxidation in open vessels.

Yin et al. [36] described the ICP–MS determination of Li, V, Cr, Co, Ga, Rb, Sr, Cd, Cs, Ba, Pb, U, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y with limits of detection ranging from 9×10^{-10} to 2×10^{-7} wt %. However, this list does not include impurities of the most common elements (Al, Ca, Mg, Si, Fe, Na, K, Zn, etc.).

Spectroscopic methods are widely used for the determination of As, Se, and Te impurities. An analyzed sulfur sample is converted into a solution (typically by the action of nitric acid), and the impurities of interest are converted into colored compounds with an organic reagent. These compounds are then extracted and determined by spectrophotometric methods. The achieved limits of detection for arsenic and selenium impurities fall within the range 10^{-6} to 10^{-5} wt % [32].

Malyshev et al. [37] presented a method for chemical–atomic absorption determination of As, Sb, and Se impurities in high-purity sulfur. They were extracted from sulfur and then determined in an aqueous solution or in toluene. The limits of detection for these elements were 1×10^{-7}, 2×10^{-7}, and 3×10^{-7} wt %, respectively.

Arsenic and selenium with a limit of detection of 1×10^{-6} wt % were determined by X-ray fluorescence spectrometry with impurity preconcentration [38].

The test sulfur sample was dissolved in nitric acid, and the solution was evaporated to dryness. The resulting precipitate, containing arsenic and selenium oxides, was applied to filter paper, which was then subjected to analysis.

In several studies [29, 31, 32], the polarographic determination of selenium up to 1×10^{-3} wt % was described, based on the facile electroreduction of selenite ions on a mercury drop electrode.

Phosphorus, with a limit of detection of 1×10^{-5} wt %, can be determined by the turbidimetric method [21]. Halogens in sulfur were determined by the light scattering method [21]. To achieve this, ethyl alcohol and water were sequentially added to a flask containing sulfur. The contents were brought to a boil, and then the resulting solution was separated from the undissolved precipitate. Nitric acid was added to the solution, followed by boiling, and then silver nitrate was added. The concentration of halogens was determined from the light scattering of the resulting solution. The application of this approach enables the determination of halogens in sulfur up to 2×10^{-5} wt %.

A highly sensitive method for determining impurities in high-purity sulfur is radioactivation analysis, which is not associated with pre-enrichment of the sample, leading to the absence of a blank correction. A procedure was described for determining 14 elements in high-purity sulfur with limits of detection for Mn, Cu, As of $(2–5) \times 10^{-8}$ wt %, Ga, Te, Sb, In, Co $(1–6) \times 10^{-7}$ wt %, Ag, Hg, Cr $(2–5) \times 10^{-6}$ wt %, and Zn, Ni, and Se $5 \times 10^{-6}–2 \times 10^{-5}$ wt % [32]. Unfortunately, this method is currently rarely used due to the limited availability of analytical equipment.

To obtain high-purity sulfur, chemical, distillation, and crystallization methods, as well as their combinations, are employed. High-purity quartz glass serves as the primary material for the apparatus used in the production of high-purity sulfur. All sulfur samples purified by high-temperature methods exhibit elevated silicon concentrations due to the formation of silicon sulfides from the sulfur melt reacting with the apparatus walls [11]. Unfortunately, silicon typically does not fall within the range of detectable impurities in most of the known sulfur analysis procedures, usually due to relatively high levels of contamination in the course of sample preparation. Nevertheless, Pimenov et al. [39] have demonstrated that during autoclave digestion of sulfur samples in vessels made of high-purity fluoroplastic using unboiled distilled nitric acid, silicon can be determined with a limit of detection of 2×10^{-5} wt %, along with impurities such as Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Ge, In, K, La, Li, Mg, Mn, Na, Nb, Ni, P, As, Rb, Sb, Sc, Se, Sn, Sr, Ta, Te, Ti, Tl, V, W, Y, Zn, and Zr, by the ICP–AES with the limits of detection ranging from 5×10^{-8} to 7×10^{-5} wt %.

DETERMINATION OF MOLECULAR IMPURITIES

Molecular impurities in sulfur serve as a significant source of contamination, diminishing the quality of sulfur-containing materials. For instance, in glass-based optical fibers with As_2S_3 the main intensely absorbing impurities are compounds of carbon, oxygen, and hydrogen. To minimize optical losses, their permissible concentrations in such glasses should not exceed $1 \times 10^{-7}–1 \times 10^{-6}$ at % [18]. Sulfur, as a component of arsenic-sulfide glasses, is the primary source of these substances. An analysis of samples of commercially available high-purity sulfur reveals that the primary chemical forms of carbon- and hydrogen-containing impurities in sulfur are hydrocarbons of varying chain lengths, and also hydrogen sulfide, carbon disulfide, and sulfur dioxide [40].

The molecular impurity composition of sulfur is complex and diverse [41]. Impurities in sulfur can be roughly divided into several groups: those with low molecular weights, with a mass of approximately 400, resins with molecular weights of about 1000, and asphaltenes with molecular weights of several thousand Da [22, 41]. These compounds belong to the class of hydrocarbons, their thio- and nitrogen derivatives, and may also be products of the cracking and sulfuration of these substances. The challenge in their determination lies in the difficulty of identifying the components that form these groups of compounds. Information regarding the exact composition and structure of such compounds in sulfur was not found in our research.

Because of the complex impurity composition of sulfur, approaches related to determining the total concentration of carbon-containing compounds, which are independent of their form, have found wide applications to sulfur analysis.

In [42], sulfur was boiled in a glass test tube for 2–3 min to determine carbon-containing impurities. Upon cooling and solidification, dark spots appeared on its surface, the areas of which were used to estimate the total concentration of carbon-containing substances. This method allows for monitoring the total organic content in sulfur at levels up to 4×10^{-2} wt %.

A method was proposed involving the dissolution of sulfur in oleum at temperatures up to 100°C [43]. During this process, the sulfonation of organic substances occurs, giving compounds with varying degrees of color intensity depending on their concentration. The impurities were determined by a photometric method. The concentration of organic substances was estimated based on the found carbon concentration. This method allows for the determination of the concentration of carbon-containing substances at levels up to 10^{-3} wt %.

In another study [21], sulfur was burned in a porcelain crucible to determine bitumens. After removing the sulfur, the bitumens remained as a dark spot at the bottom of the crucible, which were then dissolved in sulfuric acid. The total concentration of these compounds was determined based on the intensity of color of the resulting solution. This method enables the assessment of bitumen concentration at levels up to 2×10^{-3} wt %.

In [44], for the determination of bitumens, a sulfur sample weighing 2–5 g was melted and completely vaporized. The nonvolatile residue was dissolved in nitric acid, evaporated to dryness, and dissolved in sulfuric acid. Subsequently, the resulting solution was colored yellow-brown. The integral concentration of bitumens was determined by the color intensity of the solution using colorimetric methods. This technique allows for the limit of detection for bitumens to reach 4×10^{-5} wt % with a sample mass of 25 g.

Methods involving the conversion of carbon-containing impurities into carbon dioxide with the subsequent determination and assessment of the total concentration of the oxidized substances have found broader applications for the determination of carbon-containing impurities.

Murphy et al. [45] proposed the determination of carbon-containing impurities by burning a sulfur sample with the subsequent absorption of the resulting carbon dioxide gas by sodium hydroxide and its gravimetric determination. Another method for determining carbon dioxide is its absorption by ammonia solution, with the amount determined by the degree of turbidity of the resulting solution. In [46], total carbon in sulfur was determined by combustion upon heating in a stream of oxygen. The resulting sulfur oxides were absorbed by solutions of chromic and sulfuric acids. Carbon dioxide was absorbed by a barium hydroxide solution, followed by determination using titration. The limit of detection for carbon-containing substances is found to be 5×10^{-3} wt %.

Feher et al. [47, 48] converted carbon-containing compounds into carbon dioxide by sulfur oxidation in an oxygen stream. Sulfur dioxide was separated by passing it through a cooled solution of sulfuric acid and hydrogen peroxide. Carbon dioxide was determined by conductometry by measuring changes in the conductivity of a sodium hydroxide solution. The limit of detection for carbon was found to be 2.4×10^{-4} wt % with a sulfur sample weight of 1 g.

In [49], a 10-g weighed portion of sulfur was placed in ampoules of a volume of 20–30 mL. Surface impurities were removed by heating to 80°C. Then, sulfur was heated to 800°C for 1 h under oxygen. The impurities were determined by gas chromatography. A stainless steel column, 25 cm × 4 mm, cooled with liquid nitrogen, was used to separate N_2 and Ar. A 4.25 m × 3 mm column packed with the Polysorb 1 adsorbent was used to separate carbon dioxide, hydrogen sulfide, sulfur dioxide, and carbon disulfide. Carbon concentration in sulfur was determined based on the found concentrations of carbon dioxide and carbon disulfide. The limit of detection for carbon in sulfur was 6×10^{-6} wt %.

Dowling et al. [50] combusted sulfur in a quartz reactor at 800°C. Sulfur compounds were removed from the gas sample by passing it through a trap cooled to −10°C. Carbon dioxide (CO_2) determination was carried out using a gas chromatograph with a thermal conductivity detector. A column of 1.8 m × 2 mm packed with the Chromosorb 108 adsorbent was used to separate the components of the mixture, including O_2, SO_2, and CO_2. The limit of detection for carbon-containing substances was 1.5×10^{-3} wt %.

In [51], sulfur weighing 0.1–0.5 g was placed in a quartz mass spectrometric ampoule, evacuated, and then heated to 750°C for 3 h. During this process, impurities in the form of hydrocarbons, upon interaction with sulfur, were converted into CS_2 and H_2S. The presence of molecular oxygen, SO_2, and H_2O in the sulfur, along with carbon-containing substances, led to the formation of carbon dioxide (CO_2). The resulting gases from the sample were extracted under vacuum and analyzed by gas chromatography. A column of a length of 2 m packed with the Silokhrom C-80 adsorbent was used to separate these substances. The concentrations of CS_2 and CO_2 formed were used to calculate the carbon content of the sulfur. The limit of detection for carbon-containing substances in a sample weighing 1 g was 1×10^{-5} wt %.

Sukhanov et al. [52] determined the total carbon in sulfur. A sample weighing 0.1–1.5 g, together with 0.025 g of freshly calcined CuO, was placed in a preheated quartz ampoule. The ampoule was evacuated and subjected to heating at 800°C for 4 h. The oxidation products were transferred to an intermediate ampoule cooled with liquid nitrogen and then to a cuvette for the IR spectroscopic determination of carbon dioxide. The limit of detection for total carbon in the sulfur was 3×10^{-5} wt %.

The development of methods for the deep purification of sulfur greatly depends on information about specific impurities present in it. Therefore, the determination of individual substances in sulfur is an important task.

For example, Adamchik et al. [53] used IR spectrometry to identify impurities. Molten sulfur was obtained at a temperature of 125°C, revealing impurities such as CS_2, H_2S, and aliphatic hydrocarbons. The limit of detection for hydrocarbons was determined to be 2×10^{-5} wt %. In [54], a sulfur sample weighing 0.39 g was pressed into tablets, and impurities were determined by Fourier-transform IR spectrometry. Impurities including H_2S, CS_2, and hydrocarbons were identified, with limits of detection for impurities reaching 1×10^{-4} wt %.

The concentration of hydrogen, which is part of impurities of organic substances, was determined

Table 2. Impurities identified in sulfur [7, 40, 58, 59]

Compounds	Impurities
Permanent gases	N_2, Ar, O_2, CO_2, N_2O
Hydrocarbons	C_2H_2, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_8 1-butene, C_4H_8 2-butene, C_4H_8 1-propene-2-methyl, *n*-C_4H_{10}, *iso*-C_4H_{10}, C_5H_{10} 1-pentene, C_5H_{10} 1-butene-2-methyl, C_5H_{10} 2-pentene, C_5H_{10} 2-butene-2-methyl, *n*-C_5H_{12}, C_6H_6, C_6H_{12} cyclohexene, *n*-C_6H_{14}, C_6H_{12} 1-hexene, C_7H_8 toluene, C_7H_{14} 1-heptene, *n*-C_7H_{16}, C_8H_{16} 2-octene, C_8H_{16} 3-octene, C_8H_{16} 4-octene, *n*-C_8H_{18}
Oxygen-containing hydrocarbons	$C_2H_4O_2$ methylformate, C_2H_6O acetaldehyde, C_2H_6O dimethylether, C_3H_6O propanal, $C_3O_2H_6$ methylacetate, C_4OH_8 propanal-2-methyl, C_4H_4O furan, C_4H_8O 2-butanone, $C_4H_8O_2$ methylpropionate, $C_4H_8O_2$ methylmethacrylate, $C_5H_{10}O$ 3-methyl-butanal, $C_5H_{10}O$ 2-methyl-butanal, $C_5H_{10}O_2$ methyl-2-methylpropionate
Nitrogen-containing hydrocarbons	C_3H_5N propanenitrile, C_2H_3SN isothiocyanatomethane, C_2H_3N acetonitrile
Sulfur-containing substances	COS, H_2S, CS_2, SO_2, C_4H_4S thiophene, C_5H_6S 2-methylthiophene, C_5H_6S 3-methylthiophene

in [55]. To achieve this, a sulfur sample weighing 1 g was placed in an ampoule, sealed, and maintained at 500°C for 6 h. The hydrogen sulfide formed during pyrolysis reacted with an iodine solution. The excess iodine was titrated to estimate the concentration of hydrogen in the sulfur. This procedure enables the determination of hydrogen at levels up to 10^{-2} wt %.

Gas chromatography was employed for impurity determination in [56]. Sulfur was placed in a quartz ampoule and heated to 150°C. The impurities released from the melt were preconcentrated on an adsorbent with 3A molecular sieves at a liquid nitrogen temperature. Upon the completion of extraction, the impurities from the adsorbent were transferred to an ampoule, diluted with helium, and analyzed. A pyroelectric catalytic detector was used for recording permanent gases and carbon dioxide, while a flame photometric detector was utilized for sulfur-containing substances, and a flame ionization detector was used for hydrocarbons. In the high-purity sulfur sample 16-5, impurities of nitrogen, oxygen, carbon monoxide, hydrogen sulfide, carbonyl sulfide, and sulfur dioxide were determined. Their limits of detection for a 1-g sample were 1×10^{-7}, 1×10^{-7}, 4×10^{-8}, 8×10^{-9}, 3×10^{-9}, and 9×10^{-8} wt %, respectively.

In [57], impurities of benzothiophenes were identified in the sulfur sample. Sulfur was dissolved in a sodium sulfide solution followed by liquid-phase extraction to preconcentrate the impurities. Separation was carried out using a DB-5ms column (30 m × 0.32 mm × 0.25 μm), and detection was performed using a flame photometric detector. Gas chromatography–mass spectrometry was employed for identification. Impurities of benzothiophene, dibenzothiophene, and 4,6-dimethyldibenzothiophene were detected, with limits of detection of $(2–8) \times 10^{-5}$ wt %.

Impurities in the sulfur obtained from hydrocarbon gases by oxidizing the hydrogen sulfide present in them on bauxite catalysts [40] and in sulfur sample 16-5 [58, 59] were determined by gas chromatography–mass spectrometry. Sample preparation involved the extraction impurities from the molten sulfur during its complete vacuum distillation. The extracted impurities were condensed in an ampule made of molybdenum glass, cooled with liquid nitrogen. For the chromatographic separation of impurities, a GS-GasPro capillary column (60 m × 0.32 mm) with modified silica as an adsorbent and a column with the polytrimethylsilylpropyne adsorbent (25 m × 0.26 mm, $d_f = 0.25$ μm) were used. The presence of 51 impurity substances in the sulfur was found. Among them were permanent gases, thiophenes, oxygen- and nitrogen-containing substances, saturated, unsaturated, and aromatic hydrocarbons $C_2–C_8$. Concentrations of most of these substances were found in [58], ranging from 10^{-3} to 10^{-8} wt %.

The impurity composition of the ^{32}S and ^{34}S isotopically enriched sulfur, obtained by the plasma chemical reduction of $^{32}SF_6$ and $^{34}SF_6$ [60], was investigated [7]. Sample preparation also involved the extraction of impurities from the molten sulfur during distillation. Using gas chromatography–mass spectrometry, impurities such as atmospheric gases, hydrocarbons $C_3–C_6$, and sulfur-containing gases were identified. Their concentrations ranged from 10^{-7} to 10^{-5} wt %.

The application of gas chromatography–mass spectrometry to sulfur analysis has significantly expanded the information about the nature of impurities present in it (Table 2). Table 2 shows that more than 50 impurity substances belonging to various classes of compounds were found in the sulfur.

DETERMINATION OF HETEROPHASE IMPURITY INCLUSIONS

Information about the impurities in sulfur is limited due to the difficulty in determining their concentrations and sizes. Heterogeneous particles primarily consist of carbon and sulfur compounds with metals [61]. Silicon dioxide in the form of heterogeneous inclusions significantly affects the transparency of sulfur-containing glasses. These inclusions must be monitored, and their concentrations in high-purity sulfur should not exceed 10^{-7} wt % [19].

In [62], laser ultramicroscopy was used to determine heterophase inclusions. Sulfur, contained in a glass ampoule with a square cross-section, was melted at 120–125°C. The effective diameter of the particles being measured ranged from 0.08 to 0.3 μm. The range of detectable concentrations was 2×10^3–5×10^7 particles/cm^3. The impurity composition of sulfur from the specified source was characterized. The particle content of it was at the level of $n \times 10^6$ cm^{-3}. Their average diameter was 0.09 μm, with a maximum of 0.15 μm.

In [61], particle determination was based on laser ultramicroscopy. Sulfur was placed in a molybdenum glass cell with flat-parallel walls and melted at 150°C. The limit of detection for particles was 0.04 μm, with a detectable concentration range from 10^3 to 10^8 cm^{-3}. High-purity sulfur 16-5 was analyzed, revealing that the numerical concentration of particles larger than 0.04 μm exceeds 10^8 cm^{-3}.

CONCLUSIONS

The literature accumulated extensive data on methods and techniques for monitoring impurities of elements, molecular substances, and heterophase inclusions in sulfur. Various methods for detecting impurities, their analytical characteristics, and application features were described. Currently, over 40 impurity elements and more than 50 molecular substances are determined in high-purity sulfur. Elemental control is conducted at levels ranging from 10^{-10} to 10^{-5} wt %, while molecular compounds are monitored within the range 10^{-9} to 10–5 wt %. Heterophase inclusions with diameters up to 0.04 μm are monitored in concentrations ranging from 10^3 to 10^8 cm^{-3}. Advancements in the capabilities of high-sensitivity sulfur analysis methods are related with the development of analytical equipment, application of new approaches to impurity detection, and enhancement of the resolution and selectivity of the detection methods, as well as the advancement of substance preconcentration methods [1, 63].

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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