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SULPHUROUS WATERS: A NATURAL TREASURE TO BE EXPLOITED

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INTRODUCTION

Sulfurous waters are a valuable natural resource, traditionally employed for therapeutic purposes due to their beneficial effects on the skin, respiratory system, and musculoskeletal health. However, their use is often geographically limited, seasonal, and constrained by accessibility, leading to a significant portion of this resource remaining underutilized or wasted. This not only represents a loss of water but also of the dissolved chemical compounds it contains, particularly elemental sulfur and sulfur-based gases (e.g., H_2S, SO_2), which are potentially recoverable and of industrial interest.

Within the framework of circular economy principles and environmental sustainability, it is essential to investigate alternative uses of sulfurous waters that maximize resource efficiency and minimize environmental impact. The present study addresses this challenge by proposing a scientific approach for the selective recovery of sulfur and volatile sulfur compounds from sulfurous waters. This strategy not only mitigates the release of potentially harmful substances into the environment but also enables the recovery of raw materials that can be repurposed in industrial, agricultural, or energy sectors, thereby enhancing the economic and environmental value of a resource that is currently only partially exploited.

RESEARCH PURPOSES

To study the possibility of using natural sulphurous waters and hydrogen sulphide in which they are rich, to:

1] *Check for the presence of sulphides in the waters*
2] *Precipitate heavy metal ions in the form of insoluble sulphides*
3] *Extract hydrogen sulphide from sulphurous waters and use it for organic syntheses*
4] *Recovering sulphur that would otherwise be lost*
5] *Block and eliminate free radicals*

GENERAL CHARACTERISTICS OF SULPHUR AND HYDROGEN SULPHIDE

Sulphur is present in some compounds[1] such as:
[1] sulfuric acid H_2SO_4 (ℓ); [2] sulphur dioxide SO_2 (g); [3] aluminium sulphate $Al_2(SO_4)_3$(s);
[4] ammonium sulphate $(NH_4)_2SO_4$ (s); [5] sodium sulphate anhydrous Na_2SO_4(s) and decahydrate $Na_2SO_4 \bullet 10\ H_2O$(s); [6] carbon disulfide CS_2 (ℓ).

Note:
✓ Ksp is the solubility product[2]
✓ The compound H_2S is usually called *hydrogen sulphide*[3] but can also be called *sulfan*[4] and is spelled SH_2 by this name.

Hydrogen sulphide is a highly poisonous gas[5]*, and all operations with the gas must be conducted under an extractor hood. Every precaution must be observed to prevent the escape of hydrogen sulphide into the laboratory environment*.

Hydrogen sulphide can burn in contact with some metal oxides, such as barium peroxide, lead dioxide, sodium peroxide, etc. In the presence of air, contact with mixtures of calcium oxide or barium oxide and other oxides can cause a lively glow or explosion[6].

The verification of the presence of sulphides in sulphurous water was carried out on a sample of a few mL (milli litres) of sulphurous water, acidified with a few drops of HCl 6M; the reaction takes place:

$S^{2-}(aq) \quad + \quad 2HCl\,(aq) \quad \rightarrow \quad H_2S\,(g) \quad + \quad 2\,Cl^{-}(aq)$ [1]

Hydrogen sulphide gas (H_2S) (rotten egg smell) develops. A lead acetate paper, immersed in sulphurous water, blackens due to the formation of black or metallic blue PbS[7]:

$H_2S(g) \quad + \quad Pb\,(OOC{-}CH_3)_2\,(aq) \quad \rightarrow \quad PbS\,(s)$ (black) $+ \quad 2H_3CCOOH\,(aq)$ [2]

Hydrogen sulphide Lead Acetate Lead Sulphide Acetic Acid

USES OF HYDROGEN SULPHIDE

1] *Hydrogen sulphide is used for the precipitation of heavy metal ions* (Ag^{+}, Cd^{2+}, Pb^{2+}, Hg^{2+},..) *as insoluble sulphides*.[8]

Silver Ion **Ag^{+}**

$2AgNO_3\,(aq) \quad + Na_2S\,(aq) \quad \rightarrow \quad Ag_2S$[9] (solid brown to black) $+ 2NaNO_3\,(aq)$ [3]

Ksp[10] di $Ag_2S = 1.6 \times 10^{-49}$

Mercury Ion **Hg^{2+}**

The Hg^{2+} ion, in the form of chloride ($HgCl_2$), reacts with H_2S: a white precipitate is formed: $Hg_3S_2Cl_2$[11] which with other hydrogen sulphide forms black mercury sulphide[12]:

Reactions:

$3\,HgCl_2\,(aq) \quad + \quad 2H_2S\,(g) \quad \rightarrow \quad Hg_3S_2Cl_2\,(s) \quad + \quad 4HCl\,(aq)$ [4]

$Hg_3S_2Cl_2\,(s) \quad + \quad H_2S\,(g) \quad \rightarrow \quad 3HgS\,(s) \quad + \quad 2HCl\,(aq)$ [5]

Sum of [5] and [6] and, subsequent simplification:

$HgCl_2\,(aq) \quad + \quad H_2S\,(g) \quad \rightarrow \quad HgS\,(s) \quad + \quad 2HCl\,(aq)$ [6]

Ksp[13] di $HgS = 4 \times 10^{-54}$

Lead Ion **Pb^{2+}**

The lead ion reacts with H_2S to give a black precipitate of lead sulphide PbS. The precipitate is often red in the presence of hydrochloric acid, due to the initial formation of lead sulphur-chloride [Pb_2SCl_2 also written as $PbS \bullet PbCl_2$][14] which is decomposed by dilution and the passage of an excess of hydrogen sulphide to form lead sulphide [PbS][15]:

$2PbCl_2\,(s) \quad + \quad H_2S\,(g) \quad \rightarrow \quad Pb_2SCl_2\,(s) \quad + \quad 2\,HCl\,(aq)$ [7]

$Pb_2SCl_2\,(s) \quad + \quad H_2S\,(g) \quad \rightarrow \quad 2PbS\,(s) \quad + \quad 2HCl\,(aq)$ [8]

Hydrogen sulphide reacts with lead acetate to give lead sulphide, black. This reaction is used for the preparation of the lead sulphide indicator paper for the hydrogen peroxide test.[16]

The reactions involved are:

$H_2S(g) \ + \quad Pb\,(OOC{-}CH_3)_2(aq) \quad \rightarrow \quad PbS\,(s)$ (nero) $+2CH_3COOH\,(aq)$ [9a]

$PbS(s) \ + \quad 4H_2O_2(aq) \quad \rightarrow \quad PbSO_4(s) \quad + \quad 4H_2O(l)$ [9b]

A drop of the neutral or slightly acidic solution is placed on the lead sulphide (brown) paper: a white spot is obtained on the indicator paper, since the lead sulphate $PbSO_4$ formed is white. This indicates the presence of hydrogen peroxide in the sample.

The solubility product of lead sulphide (PbS) is Ksp[17]=5x10—29 Lead sulfide precipitate is soluble in hot dilute nitric acid (HNO_3)[18]:

$3PbS + 8HNO_3$ $3Pb(NO_3)_2 + 2NO + 4H_2O + 3S$ [10]

Chromium ion $\mathbf{Cr^{3+}}$

The chromium ion reacts with H_2S to give chromium sulphide: brownish Cr_2S_3 (black)[19]. The sulphide is hydrolyzed in aqueous solution to give the hydroxide $Cr(OH)_3$ (gelatinous solid whose colour can be from gray–green to gray–blue[20].

Reactions

$2CrCl_3\,(aq) + 3H_2S\,(g)$ $Cr_2S_3\,(s) + 6HCl\,(aq)$ [11]

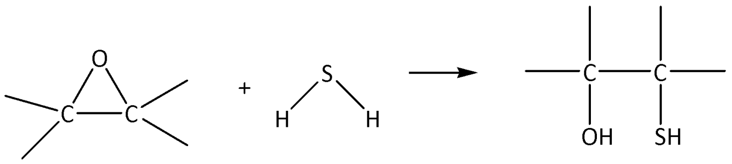
$Cr_2S_3 + 6H_2O$ $2Cr(OH)_3 + 3H_2S$ [12]

{Ksp di $Cr(OH)_3$}[21] = 2.9×10^{-29}

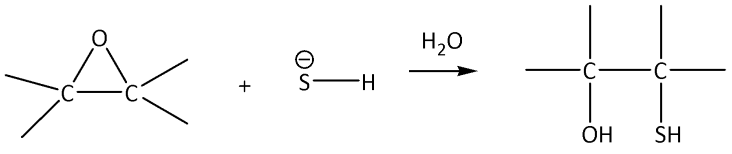
2] *Hydrogen sulphide is used for organic syntheses* (some examples are shown below):

When epoxides are the substrates that react with hydrogen sulphide, the products that are obtained are β-hydroxy-thiols[22]: [$^{(\beta)}$C(OH)—$^{(\alpha)}$C(SH)].

Reaction [14]



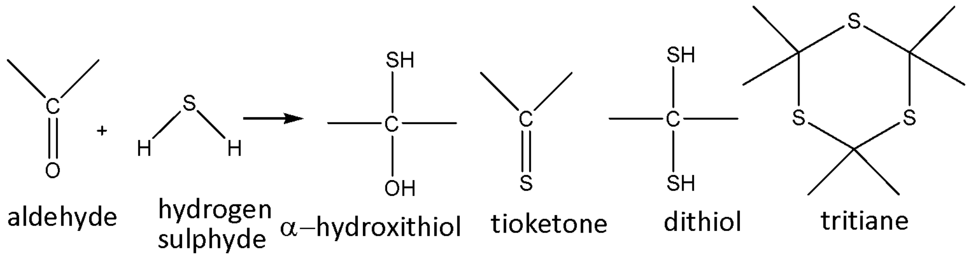
Reaction [15]



Epoxido Sulphydrate β-Hydroxy-thiol

The reaction [15] is the same reaction [14] but with the hydrogen sulphide ion ($^-$SH) instead of H_2S. The addition of H_2S to carbonyl compounds such as aldehydes and ketones produces various products. The most usual is *tritian*. The reaction is called O-hydro-C-mercapto-addition:

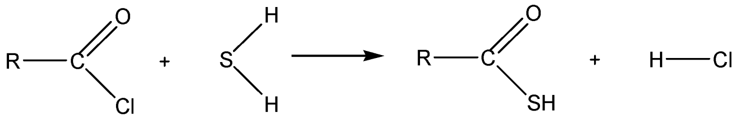
Reaction [16]



Hydrogen sulphide is used in the mercapto-de-halogenation reaction[23]: H_2S attacks alkyl carbon to form thiols (RSH) [reactions 14-15-16]. The term thiol derives from the prefix tio[24], from the Greek thêion which means sulphur and from the ending olo[25] which characterizes alcohols (methanol, ethanol, etc.); the SH group is analogous to the OH group.

$$RX + H_2S \rightarrow RSH_2^+ + X^- \qquad [17]$$
$$RSH_2^+ \rightarrow RSH + H^+ \qquad [18]$$
$$RX + HS^- \rightarrow RSH + X^- \qquad [19]$$

H_2S is used in mercapto-de-halogenation on an acyl carbon[26]: a Thiol-Acid is formed:



[20]

Mercapto-de-diazoniation[27]

$$ArN_2^+ + HS^- \rightarrow ArSH + N_2 \qquad [21]$$
$$2ArN_2^+ + S^{2-} \rightarrow ArSAr + 2N_2 \qquad [22]$$

RESEARCH OBJECTIVES

1] *Hydrogen sulphide can reduce chemical species*

It reduces potassium permanganate in acidic solution [*reaction 1*][28]

$$2KMnO_4\ (aq) + 5H_2S\ (g) + 3H_2SO_4(aq)\ (K_2SO_4\ (aq) + 2MnSO_4\ (aq) + 8H_2O(l) + 5S\ (s) \qquad [23]$$

It reduces potassium dichromate in acidic solution [*reaction 2*][29]

$$K_2Cr_2O_7\ (aq) + 3H_2S(g) + 4H_2SO_4\ (aq) \rightarrow Cr_2(SO_4)_3\ (aq) + 3S\ (s) + K_2SO_4\ (aq) + 7H_2O\ (l) \qquad [24]$$

It reduces elemental Iodine in acidic solution [*reaction 25*]30]

$$I_2(aq) + H_2S\ (g) \rightarrow 2HI\ (aq) + S(s) \qquad [25]$$

2] *Precipitate heavy metal ions in the form of insoluble sulphides* [31]

Examples:

Silver [Ag^+]: $Na_2S + 2AgNO_3 \rightarrow Ag_2S\ (Kps=1.6x10^{-49}) + 2NaNO_3$ [26]

Mercury [Hg^{2+}]: $H_2S\ (g) + HgCl_2\ (aq) \rightarrow HgS\ (s) + 2HCl\ (aq)$ [27]
$Ksp=4x10^{-54}$

Lead [Pb^{2+}]: $H_2S\ (g) + Pb(NO_3)_2 (aq) \rightarrow PbS\ (s) + 2HNO_3\ (aq)$ [28]
$Ksp=5x10^{-29}$

3] *Hydrogen sulphide could block and could eliminate free radicals*.

Thiols are very effective hydrogen donors and react quickly with free radicals[32] as molecules (•NO, •NO_2 etc....) or fragments of molecules (HO•, H_3C• etc.); both types have an unpaired electron.

The mechanism could be:

$R'SH + R\bullet \rightarrow RH + R'S\bullet$ [29]

By analogy with the reaction of thiols with free radicals, H_2S reactions with free radicals could also occur [see reaction by means of DPPH, hereinafter in the test]:

$H_2S + R\bullet \rightarrow RH + HS\bullet$ [30]
$HS\bullet + R\bullet \rightarrow RSH$ (thiol) [31]

HYDROGEN SULPHIDE AND PICTORIAL PIGMENTS

Hydrogen sulphide (H_2S) interacts with the pictorial pigments containing metals: lead from white lead, silver leaf, etc., with which it forms black sulphides. Some pigments containing sulphides tend to react with lead-based and copper-based pigments to form dark-coloured sulphides[33].

ORIGIN OF HYDROGEN SULPHIDE

Hydrogen sulphide is often present in groundwater and is common in wastewater. Most of it comes from the reduction of sulphates (SO_4^{2-}) by bacteria. H_2S is very toxic and has caused numerous fatalities among workers in the sewers.[34]

The anions derived from H_2S are HS^- [hydrogen sulphide (1−)][35] and S^{2-}[sulphide][36]. Hydrogen sulphide is also a common pollutant produced by volcanoes, tanning factories, pulp factories and paper factories[37] derived from wood. Dissolved organic matter in water can decompose under *aerobic* conditions[38] [conditions in the presence of oxygen]. Organic matter can also undergo decomposition under anaerobic conditions [anaerobic degradation of organic substances in the absence of oxygen]. The anaerobic sulphate-reducing bacterium, Desulfovibrio[39] reduces the aqueous sulphate to hydrogen sulphide (H_2S).

Hydrogen sulphide exists in different molecular forms called **polysulphides** as described below[40]:

H_2S sulphide (colourless gas)–H_2S_2 disulphide (yellow oil)–H_2S_3 trisulphide (yellow-brown liquid)–H_2S_4 tetrasulphide (bright yellow)–H_2S_5 pentasulphide (light yellow).

HYDROGEN SULPHIDE (H_2S) IN AQUEOUS SOLUTION AND DISSOCIATION CONSTANTS[41]

In aqueous solution, hydrogen sulphide dissociates and ionizes according to the reactions:

$H_2S(g)$ + $H_2O(l)$ $HS^-(aq)$ $+H_3O^+(aq)$ K_1 (18°C) = $9.1 \bullet 10^{-8}$ $pK_1 = 7.04$ [32]

$HS^-(aq)$ $+H_2O(l)$$S^{2-}(aq)$ $+H_3O^+(aq)$ K_2 (18°C) = $1.1 \bullet 10^{-12}$ $pK_2 = 11.96$ [33]

K1 and K2 are the dissociation constants whose values have been acquired from "Dissociation Constants of Inorganic Acids in Aqueous Solutions" (Approximately 0.10–01 N) in CRC, Handbook of Chemistry and Physics 68th edition, D-163, 1987-1988).

4] *Recovery of sulphur from hydrogen sulphide*

The considerable amounts of hydrogen sulphide recovered from oil and natural gas are often transformed into solid elemental sulphur, by means of the Claus process[42] in the gaseous phase where one-third of the amount of hydrogen sulphide extracted from fossil fuels is burned to sulphur dioxide to obtain the second reactant (SO_2) of this process:

$2H_2S(g)$+ $3O_2(g)$ $2SO_2(g)$ + $2H_2O(g)$ [34]

The process is completed by means of the reaction:

$2H_2S(g)$+ $SO_2(g)$ $3S(s)$ + $2H_2O(g)$ [35]

Hydrogen sulphide is oxidized in the atmosphere[43] first, partially, to sulphur dioxide (SO_2) [reaction 36] and then completely to sulfuric acid (H_2SO_4) or sulphate ion (SO_4^{2-}) [reaction 37]. The possible reactions that interpret the oxidation processes described, are shown below:

$2H_2S(g)$+ $3O_2(g)$ $2SO_2(g)$ + $2H_2O(g)$ [36]

$2SO_2(g)$ + $2H_2O(l)$ + $O_2(g)$ $2H_2SO_4(l)$ [37]

The reaction [36] is the same as the reaction [34] and the reaction [37] is the synthesis of some reactions that are described in the process of "oxidation of SO_2 in the atmosphere: the mechanism in the homogeneous gas phase" of the text Environmental Chemistry by Colin Baird cited in the bibliography.

WATER CONDITIONS OF A LAKE[44]

The water on the surface of a lake, rich in oxygen, is in aerobic conditions; the chemical elements (C, S, N,) are in their most oxidized form: CO_2 or H_2CO_3 or HCO_3^-, SO_4^{2-}, NO_3^-, Fe $(OH)_3$ insoluble. In the seabed, the water is poor in O_2 as it is consumed during the decomposition of biological material. The conditions are anaerobic, the various elements are in their most reduced form such as: CH_4, H_2S, NH_3 and NH_4^+, soluble Fe^{2+}. *Hydrogen sulphide dissolved in water* can be incompletely oxidized by some elemental sulphur bacteria or entirely to sulfuric acid[45].

Oxidation reactions are:

$2H_2S(g)$+ $O_2(g)$ $2S(s)$ + $2H_2O(l)$ [38]

$$H_2S(g) + 2O_2(g) \rightarrow H_2SO_4(g) \qquad [39]$$

PREPARATION OF HYDROGEN SULPHIDE

Hydrogen sulphide can be prepared, in the laboratory, from iron sulphide (FeS), called *natural troilite*[46], and iron disulphide (FeS_2), called *pyrite*[47], reacted with dilute hydrochloric acid [example: HCl diluted 1:3 (one to three); meaning that a volume of concentrated HCl (37.27% by mass; density=1.185 g/mL)[48] is diluted to a volume three times greater.

Reactions

$$FeS(s) + 2HCl(aq) \rightarrow 2H_2S(g) + FeCl_2(aq) \qquad [40]$$

$$FeS_2(s) + 2HCl(aq) \rightarrow 2H_2S(g) + FeCl_2(aq) \qquad [41]$$

From an analytical point of view, three categories of sulphide in water and wastewater are distinguished[49]:

a *Total sulphide*: includes dissolved H_2S and HS^-, as well as metal sulphides (soluble in acids) present in the suspended material. The S^{2-} ion is negligible, amounting to less than 0.5% of dissolved sulphide at pH 12, and less than 0.05% at pH 11, etc.

b *Dissolved sulphide*: it is what remains after the suspended solids have been removed by flocculation and sedimentation.

c *Non-ionized hydrogen sulphide: it can be calculated from the concentration of the dissolved sulphide, the pH of the sample, and the ionization constant of the hydrogen sulphide.*

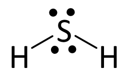
Physical and Chemical Constants of H_2S[50]

[colourless, flammable gas, density (0°) = 1,539 g/L; melting point = −85.5°C; boiling point = −60.7°C; solubility in water = 437 cm^3 at 0°C and 186 cm^3 at 40°C]; solubility in alcohol (ethanol) = 9.54 cm^3 at 20°C; H_2S is soluble in CS_2 (carbon disulphide).

Equivalent mass of H_2S.

In *neutralization reactions*, the equivalent mass of an acid[51] is the mass of an acid that contains one mole of replaceable hydrogen atoms, i.e. 1.0078 g of hydrogen. The equivalent mass of H_2S is obtained by dividing its molar mass by 2 since it can give up, overall, 2 moles of protons as expressed above in the dissociation reactions. Equivalent mass of H_2S = [Molar Mass/2] = [34.08/2] = 17.04.

MOLECULAR CHARACTERISTICS OF HYDROGEN SULPHIDE



Hydrogen sulphide is a molecule with two bonds S—H [52] whose length is 133.6 pm [1 picometer (pm)= 10^{-12} m] and bond angle of 92.10^0.

The molecular geometry is of the AX_2E_2 type[53] where: A is the central atom; X are the atoms joined by simple bonds to the central atom; E is the non-bonding electron pair or lone pair. The geometric arrangement of atoms in the molecule is deduced from the V S E P R (Valence-Shell Electron-Pair Repulsion) model[54] whose basic assumption is that "the electron pairs of the valence layer of an atom, whether ligating or non-ligand, adopt the arrangement that keeps them as far away as possible from each other; they behave, consequently, as if they were repelling each other." This arrangement of the electron pairs in the valence layer of an atom makes it possible to derive, quite easily, the geometry of the covalent bonds that the atom itself establishes.

EXPERIMENTAL PART

In this research, a dark glass bottle (V=1000 mL) of "natural sulphurous-sulphate-calcium-magnesium mineral water" was used. It is used for inhalation and nebulisation.
The Chemical and Chemical-Physical evaluations (*parameters*) shown on the bottle label[55] are shown in table 1.

Table 1

Parameters	*Declared*	*Sulphurous water pH measurement*
H_3O^+ Ion Concentration (pH)	6.7	The pH of sulphurous water is measured by means of two pH indicator papers: 1] pH range = 1÷11 2] pH range 6.5÷10. Value obtained ≈ 7 in both ways
Sulphidrometric Degree* (H_2S)	119 mg/L	
Sulfidrato (HS^-)	54 mg/L	
Non-ionized hydrogen sulphide (H_2S)	65 g/L	

* The declared sulphydrometric degree indicates the total content of hydrogen sulphide, in the two forms (H_2S + HS^-), in one litre of sulphurous water. In fact, the sum of the concentrations of the two forms is: (54 + 65) mg/L = 119 mg/L. as shown in table 1 and indicated on the bottle label.

When the bottle of sulphurous water is opened, the smell of rotten eggs, characteristic of H_2S, is immediately perceived, as this is freed from the solution and diffuses into the environment; The bottle is then closed with a colourless plastic cap. At the bottom of the bottle and on the surface of the water, a small amount of solid (more on the bottom) is observed. This is recovered by filtration of 870 mL of sulphurous water using a slow filter (*blue band*). The solid is allowed to air dry at room temperature. The solid, thus dried, is placed inside a glass tube for reactions, fixed horizontally with a metal support as shown, schematically, in the following drawing:

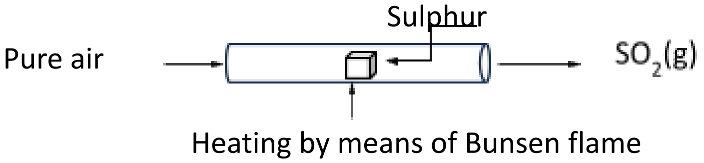


Figure 1

At one end of the tube, pure air is introduced from a cylinder, as shown in figure 1.

The solid is placed in the centre of the pipe and at the other end of the outlet, the fumes (presumably SO_2) produced by combustion, are collected, and bubbled in 25 mL of an aqueous solution of Iodine (I_2) 0.1 N, acidified with 0.5 mL of H_2SO_4 1 M. At the end of the reaction, the reddish-brown colour of equal volumes of the iodine solution is compared with that after the bubbling of the gas leaving the combustion pipe. The reddish-brown colour of the solution after the bubbling of the fumes is decidedly lighter than the colour of the comparison solution. This means that iodine has reacted with a reductant, and this can only be SO_2, produced by the combustion of the solid. The concentration of iodine decreases resulting in colour lightening because the products of the reaction are colourless. The reactions that interpret this result are[56]:

$$SO_2 + 2H_2O \rightarrow H_3O^+ + HSO_3^- \qquad [42a]$$
$$HSO_3^- + H_2O \rightarrow H_3O^+ + SO_3^{2-} \qquad [42b]$$
$$SO_3^{2-} + I_2 + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2I^- \qquad [43a]$$
$$HSO_3^- + I_2 + H_2O \rightarrow SO_4^{2-} + 3H^+ + 2I^- \qquad [43b]$$

The experiment shows that the unknown solid is *sulphur* that can have formed in the sulphurous water only by means of the reaction [38].

DETERMINATION OF THE TOTAL SULPHIDE CONTENT IN THE SAMPLE (1L) OF SULPHUR WATER

The determination of the sulphide content of sulphurous water is carried out by means of iodometric titration.[57]

The reagents required are: HCl 6N; iodine(I_2) standard solution 0.025 N; sodium thiosulfate solution ($Na_2S_2O_3$) 0.0125 N.

SULPHUROUS WATER TITRATION[58]

The solution to be titrated is prepared by placing the following reagents in a 250 mL flask: 25 mL of I_2 solution 0.025 N + 2 mL of HCl(aq) 6 N + 25 mL of sulphurous water. Four drops of 1% starch weld (m/V) are added as an indicator[59]. Titration is a retro-titration since a higher amount of I_2 is added than that necessary to react with hydrogen sulphide (H_2S). You can realize the excess iodine from the reddish-brown colour of the solution.

Reaction between iodine and hydrogen sulphide[60]:

$$I_2 + H_2S \rightarrow S + 2H^+ + 2I^- \qquad [44]$$

Excess iodine is titrated with an aqueous solution of sodium thiosulfate 0.0125 N according to the reaction:[61]

$$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI \qquad [45a]$$

or in ionic form:

$$I_2 + 2S_2O_3^{\ 2-} \rightarrow S_4O_6^{\ 2-} + 2I^- \qquad [45b]$$

Four tests are performed, the results of which are shown in table 2.

Tabella 2

Proof	V (mL) of sulphurous water	V (mL) I_2 0.025 N	V (mL) $Na_2S_2O_3$ 0.0125 N	Average V (mL) of $Na_2S_2O_3$ 0.0125 N
1	25	25	35.80	36.60
2	25	25	37.85	
3	25	25	37.10	
4	25	25	35.65	

Sulphurous water samples are taken after shaking the bottle (V = 1L) containing it to make them homogeneous. They are made acidic by adding 2 mL of HCl 6 N to each of them, since the reactions involved in the titration take place in an acidic environment, according to the method used: Titrimetric (Iodine) Method described in "Standard Methods for the Examination of Water and Wastewater, fourteenth edition 1976".

The titration of sulphurous water is carried out by means of the method of retro-titration by adding an excess of I_2 to the sulphurous water sample. A part of Iodine will react with H_2S according to the reaction [44] written above. Unreacted iodine is titrated with sodium thiosulfate ($Na_2S_2O_3$) in the presence of the starch weld indicator, according to the reaction [45a], or written in ionic form, [45b]. The addition of I_2 to sulphurous water causes turbidity because elemental sulphur is released by oxidation of H_2S (see reaction 44). The solution is also coloured light blue, due to the interaction between iodine and starch weld. When the colour disappears, it means that the point of equivalence of the titration has been reached.

CALCULATIONS

[0.0125 eq. / 1000mL] • 36.6 mL=4.575×10^{-4}=number of equivalents (eq.) of thiosulfate reacted with excess of Iodine (I_2) and corresponding to an equal number of the excess of the I_2 equivalents.

Added iodine=[0.025 eq. / 1000mL] • 25 mL= 6.25×10^{-4} = equivalents number (eq.) of I_2 in 25 mL of I_2 0.025 N added. The number of iodine equivalents reacted with hydrogen sulphide present in 25 mL of sulphurous water is given by the difference between those added and those in excess after the reaction [44]:

$(6.25 \times 10^{-4})-(4.575 \times 10^{-4})=1.675 \times 10^{-4}$ number of equivalents (eq.) of I_2 reacted with H_2S. Calculation of I_2 equivalents that reacted with H_2S in 1000 mL of sulphurous water:

$$1.675 \times 10^{-4}\text{eq.} \quad : \quad 25\text{ mL} \quad = \quad x \quad : \quad 1000\text{ mL}$$

$$X = [1.675 \times 10^{-4}\text{eq.} / 25\text{ mL}] \times 1000\text{ mL} \quad = \quad 6.7 \times 10^{-3}\text{ eq.}$$

Molar Mass of H_2S = 34.08 g/mole [62]

Equivalent Mass of H_2S = (Molar Mass / 2) = 17.04 g/eq.

The equivalent mass[63] of H_2S is equal to the molar mass divided by 2, because in acids the equivalent mass is equal to the molar mass divided by the number of hydrogen atoms that can be replaced in acid−base reactions.

Mass of H_2S in 1 L of sulphurous water=6.7×10^{-3} eq. x 17.04g x eq^{-1} = 0.114 g = 114 mg.

The mass of H_2S in 1 L of sulphurous water declared on the bottle label is 119 mg. The percentage of H_2S measured compared to the declared is:

$$[114\text{mg } L^{-1} / 119\text{ mg } L^{-1}] \times 100 = 95.80\,\% \approx 96\%$$

There is a good agreement between the result declared on the label and the measured one. However, it must be borne in mind that the declared value is obtained in a survey very distant in time compared to that currently measured. In fact, during the collection, bottling and storage of sulphurous water, part of H_2S is released from the water to become gaseous H_2S that is dispersed into the environment. In part, it oxidizes to elemental sulphur and in part it oxidizes to sulphuric acid [reactions 38 and 39], therefore, the bottled water contains a slightly lower H_2S content than that of the original source.

OZONE FORMATION

Ozone is produced in the stratosphere through the following mechanism:

if a molecule of oxygen (O_2) absorbs a photon of light of 241 nm or less, it has enough excess energy to dissociate[64]:

$O_2(g)$ + fotone UV ($\lambda<240$ nm) ⍰ $2O(g)$ [46]

The atomic oxygen produced reacts with molecular oxygen to produce ozone and heat[65]

$O_2(g)$ + $O(g)$ ⍰ $O_3(g)$ + heat [47]

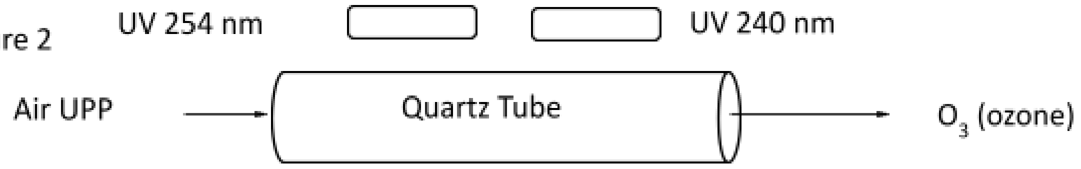
The stratospheric ozone layer shields ultraviolet light in the range of 240 to 310 nm by means of the reaction[66]:

$O_3(g)$ + photon UV [$240\text{ nm} < \lambda < 310\text{ nm}$] ⍰ $O(g)$ + $O_2(g)$ [48]

LABORATORY PREPARATION OF OZONE[67]

An ozone preparation equipment is assembled as in figure 2. The UV lamps available in the laboratory are of two different wavelengths (240 and 254 nm)

Figure 2



A quartz tube is used to prepare ozone because this material is transparent to UV radiations[68]

The reactions [46], [47] and [48] describe the formation and destruction of ozone in the stratosphere, so it is superfluous to repeat them in its preparation according to the figure 2.

AIR FLOW MEASUREMENT

The purpose of measuring air flow is to make sure that its flow is quite low so that exposure to UV radiation (figure 2) is sufficient to produce ozone.

Table 3

<table>
<tr>
<td>The flow rate of the air, which comes from a cylinder, is measured by collecting a known volume of it by means of a 1000 mL graduated cylinder whose "mouth" is immersed in water contained in a crystallizer to ensure the hydraulic seal with the cylinder filled with water. The air is introduced into the cylinder by means of a plastic tube shaped into a shape suitable for the purpose. The volume collected and the time required are measured; the flow rate in L/min is calculated. The average value of air flow rate is calculated after conducting four measurement tests.</td>
<td>Air flow rate = V (mL) / t (s)
Table 3
<table>
<tr><th>V (mL) of air</th><th>t (s)</th><th>Flow rate mL/s</th><th>Flow rate L/min</th></tr>
<tr><td>1000</td><td>419</td><td>2.3866</td><td>0.1432</td></tr>
<tr><td>400</td><td>173</td><td>2.3121</td><td>0.1387</td></tr>
<tr><td>400</td><td>176</td><td>2,2727</td><td>0.1364</td></tr>
<tr><td>400</td><td>176</td><td>2.2727</td><td>0.1364</td></tr>
</table>
</td>
</tr>
</table>

$$Average\ flow\ rate\ in\ L/min = \frac{0.1432+0.1387+0.1364+0.1364}{4} = 0.1387\ \frac{L}{min}$$

To check for the presence of ozone in the air irradiated by means of UV radiation, the presumed ozonated air is bubbled for forty-five (45) minutes in a volume of twenty-eight (28) mL of a potassium iodide (KI) solution to which ten (10) mL of sulphuric acid (H_2SO_4) diluted one to four (1:4) is added. The mixture is contained in a hundred (100) mL beaker. The colour of the solution changes from straw-yellow to intense orange. It is the clue demonstrating the formation of elemental iodine (solid iodine has a violet-black-metallic-shiny colour[69] released because of the reaction:

$$2I^{-} + O_3 + 2H^{+} \rightarrow I_2 + O_2 + H_2O \qquad [49]$$

The reaction [49] is interpreted by means of half-reactions and their standard reduction potentials $E^0(V)$[70]

$$O_3 + 2H^{+} + 2e \rightarrow O_2 + H_2O \qquad E^0=2.076 \qquad [50]$$

$$2I^{-} \rightarrow I_2 + 2e \qquad E^0=-0.5355 \qquad [51]$$

The sum of the two half-reactions is:

$$O_3 + 2H^{+} + 2e + 2I^{-} \rightarrow O_2 + H_2O + I_2 + 2e$$

Simplifying, we have:

$$O_3 + 2H^{+} + 2I^{-} \rightarrow O_2 + H_2O + I_2 \qquad [52]$$

$$\Delta E^0 = 2.076 - 0.5355 = 1.5405 \text{ V}$$

ΔE^0 is positive; it means that reaction [52] has a great tendency to take place; that is, ozone can easily oxidize the iodide ion to elemental iodine, in an acidic environment. To confirm this reaction, an aliquot of the solution is taken, and ten (10) mL of deionized water and two drops of starch weld are added[71]; a dove grey colour is obtained. This is an indication of the interaction between starch and iodine weld[72] that was released in the reaction. Simple air bubbling is used with the same quantities of reagents and the same methods of execution: the same phenomenon is achieved but the staining is less intense. The phenomenon is interpreted[73] by means of the semi-reactions [53], [54] and the overall reaction [56]:

$$O_2 + 4H^{+} + 4e \rightarrow 2H_2O \qquad E^0=1.229 \qquad [53]$$

$$2x[2I^{-} \rightarrow I_2 + 2e] \qquad E^0=-0.5355 \qquad [54]$$

$$O_2 + 4H^{+} + 4e + 4I^{-} \rightarrow 2H_2O + 2I_2 + 4e \qquad [55]$$

Simplifying, the following reaction is obtained[74]:

$$O_2 + 4H^{+} + 4I^{-} \rightarrow 2H_2O + 2I_2 \qquad [56]$$

$$\Delta E^0 = 1.229 - 0.5355 = 0.6935 \text{ V}$$

ΔE^0 is positive; it means that reaction [56] has a great tendency to take place; that is, oxygen can oxidize the iodide ion to elemental iodine, in an acidic environment. If we compare the two oxidation reactions of the iodide ion: [52] and [56], we see that [52] has a much more positive ΔE^0 than that of [56] (it is more than double). It means that between the two competing reactions, oxidation with ozone tends to be more favoured. This analysis only compares the potential for the two reactions to occur, but nothing can say about their speeds.

HYDROGEN SULPHIDE OXIDATION EXPERIMENT BY MEANS OF OZONATED AIR

The experiment of oxidation of the hydrogen sulphide (H_2S) of sulphurous water with ozonated air is carried out. This is prepared by means of the system shown in figure two (2) and carrying out the reaction in the gaseous phase. The H_2S is extracted and dragged from the sulphurous water [a hundred (100 mL)], contained in a two hundred and fifty (250) mL bubbler by means of nitrogen current, as shown in the diagram in figure four (page 16) concerning the use of H_2S for the precipitation of heavy metal ion sulphides. The gaseous stream is passed through the quartz tube which has open ends, as shown in the following drawing in figure three.

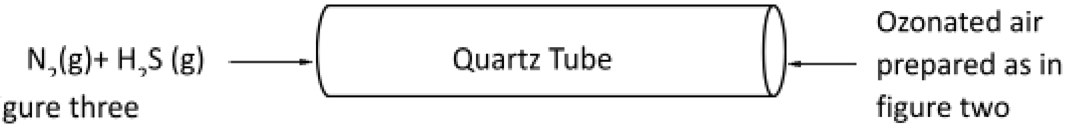


Figure three

After about forty minutes of operation of the system, no solid sulphur particles are observed along the reaction tube. It means that under the conditions adopted, the potential reaction:

$3H_2S\,(g) + O_3(g) \rightarrow 3S(s) + 3H_2O(l)$ [57]

does not happen; or it happens but at such a low speed that no change is observed during the period of operation; or not enough ozone has formed. At this point it is decided to use the alternative reaction between sulphurous water and hydrogen peroxide in an acidic environment. For this purpose, a hydrogen peroxide solution [hydrogen peroxide, 3% (three percent) H_2O_2 (m/m)] is added to an aliquot (20 mL) of sulphurous water. The hydrogen peroxide is added drop by drop until the solution becomes yellowish in colour and, subsequently, becomes cloudy with a solid suspension and whitish−yellow in colour. This behaviour is the clue that the reactions [73] [58] and [60] that lead to the formation of solid sulphur may have occurred. Sulphur is dispersed in the solution and would cause its cloudiness and whitish−yellow colour:

$H_2S\,(aq) + H_2O_2\,(aq) \rightarrow S\,(s) + 2H_2O\,(l)$ [58]
$S^{2-}\,(aq) + 4\,H_2O_2\,(aq) \rightarrow SO_4^{2-}(aq) + 4\,H_2O\,(l)$ [59]
$2H_2S\,(aq) + 4H_2O_2\,(aq) \rightarrow S\,(s) + SO_2\,(g) + 6H_2O\,(l)$ [60]
$H_2S\,(aq) + 3H_2O_2\,(aq) \rightarrow SO_2\,(g) + 4H_2O\,(l)$ [61]
$2H_2S\,(g) + SO_2(g) \rightarrow 3S(l) + 2H_2O(g)$ [62]

Reaction verification experiments [58], [59], [60], [61], [62] were not performed. However, the presence of a yellowish solid dispersed in the reaction solutions is the clue that this is elemental sulphur that may result from the reactions [58], [60] and [62]. The reaction [59], moreover, is certain as it is cited in the text "D. C. Harris, Quantitative Chemical Analysis; Freeman and Company 2010,

The reaction [59] is like to the reaction [74]:

$Na_2S(aq) + 4\,H_2O_2\,(aq) \rightarrow Na_2SO_4(aq) + 4\,H_2O\,(l)$ [63]

Hydrogen sulphide reacts with sulphur dioxide when to remove the H_2S that is produced in oil desulfurization, the same H_2S is burned in the air to produce sulphur dioxide. The latter gas then reacts with the additional hydrogen sulphide to produce sulphur, according to the reactions[75]:

$2H_2S\,(aq) + 3O_2(g) \rightarrow 2SO_2(g) + 2H_2O(l)$ (combustion) [64]
$2H_2S\,(g) + SO_2(g) \rightarrow 3S(l) + 2H_2O(g)$ [65]

These reactions are thought to be responsible for sulphur deposits around hot springs and volcanoes. The reactions [64] and [65] take place at high temperature as the H_2S (g) is burned according to the reaction [64]. It has not been proven that they can also occur at room temperature. The formation of solid sulphur at room temperature can be explained by the reactions [58] and [60]. In the light of these results, it could be hypothesized that the recovery of sulphur from sulphurous waters can be carried out precisely with reactions [58] and [60], even if a part can be lost due to reactions [59] and [61].

PREPARATION OF HEAVY METAL ION SOLUTIONS WITH A FIXED MOLAR CONCENTRATION[76].

As an example, the calculations for preparing the $HgCl_2$ solution are shown.

Molar mass of $HgCl_2$ = 271.50 g mol^{-1}

One litre of solution with Concentration = 0.025 M, contains 0.025 moles of solute, i.e.:

$$271.50\ \text{g mol}^{-1} \bullet 0.025\text{moli} = 6.7875\text{g di soluto}$$

To prepare 100 mL of 0.025 M solution, it is necessary to weigh [6.7875g/10]=0.67875g≈0.6788g of solute. The weighted masses are not always the same as those calculated; however, the very small differences recorded do not imply ambiguity or unreliability in their use.

Tabella 4

Sale (g)	Massa Molare (g)	Molarità (M) Soluzione	pH Soluzione	Volume (mL) Soluzione	Massa (g) da pesare	Massa (g) pesata
Pb $(OOCCH_3)_2 \bullet 3H_2O$	379.34	0.025	6	200	1.8967	1.8967
$HgCl_2$	271.50	0.025	6	100	0.6788	0.7416
$NiSO_4 \bullet 7H_2O$	280.88	0.025	6	100	0.7022	0.7023
$CuSO_4 \bullet 5H_2O$	249.68	0.025	6	200	1.2484	1.2484
$K_2Cr_2O_4$	194.20	0.025	8	100	0.4855	0.4855
$K_2Cr_2O_7$	294.19	0.025	6	100	0.7355	0.7356
$CoCl_2$	129.84	0.025	6	100	0.3246	0.3248
$FeSO_4 \bullet 7H_2O$	278.01	0.025	6	200	1.3901	1.3900
$AgNO_3$	169.87	0.025	6	200	0.8494	0.8495

ASSAY TO VERIFY THE PRESENCE OF H_2S IN SULPHUREOUS WATER[77]

A bottle of sulphurous water, already opened fourteen (14) days earlier and closed by means of a plastic cap, is used to check for the presence of H_2S. Three samples of fifty (50) mL each, of sulphurous water, acidified with ten (10) mL of hydrochloric acid (HCl), respectively 1 M, 2 M, 6 M. In all three cases, the lead acetate paper to check for the presence of H_2S does not blacken: the water sample does not contain H_2S. It may have evaporated or oxidized to elemental sulphur (reactions 35 and 38), which makes the water cloudy; or to have oxidized to sulphur dioxide (reactions 34 and 36), or to sulphuric acid (reactions 37 and 39). You can also experience all these situations at once. The assay is repeated with sulphurous water just opened, acidified by means of HCl 6M; the lead acetate paper blackens: PbS (black) is formed. It is an indication that the water contains H_2S.

Reactions

$S^{2-}(aq) + 2H_3O^+(aq)$ ▯ $H_2S(g) + 2H_2O(l)$ [65]

Pb $(OOCCH_3)_2(aq) + H_2S(g)$ ▯ PbS(s) (black) + $2CH_3COOH$ (aq) [66]

Experiment of precipitation of metal ions as sulphides by direct mixing of sulphurous water and solutions of the metal ion $[Me^{n+}]$[78]. The data are summarized in tables 5 and 6.

Table 5

$[Me^{n+}]$ Ion	Ion Conc. (moli/L)	V(mL) Sol. Ion	pH Sol. $[Me^{n+}]$	V(mL) Water Sulph.	pH Water Sulph.	pH Mix: Sulph.+ $[Me^{n+}]$	Precipitated sulphide: Me_2S_n [General formula]
Ag^+	0.025	20	6	10	7	6	Ag_2S grey/black
Fe^{2+}	0.025	20	6	10	7	6	FeS deep orange
Cu^{2+}	0.025	20	6	10	7	6	CuS black
Ni^{2+}	0.025	20	6	10	7	6	NiS black
CrO_4^{2-}	0.025	20	8	20	7	6	Cr_2S_3 black $[Cr(OH)_3]$
$Cr_2O_7^{2-}$	0.025	20	6	20	7	6	Cr_2S_3 black $[Cr(OH)_3]$
Hg^{2+}	0.025	20	6	10	7	6	$Hg_3S_2Cl_2$ pearl-white HgS black
Pb^{2+}	0.025	20	6	10	7	6	PbS black
Co^{2+}	0.025	20	6	10	7	6	CoS black (grains)

Table 6

Metal sulphide formation reactions

$Ag^+ + H_2S \rightarrow Ag_2S + 2H^+$	$Cu^{2+} + H_2S \rightarrow CuS + 2H^+$
$Fe^{2+} + H_2S \rightarrow FeS + 2H^+$	$Co^{2+} + H_2S \rightarrow CoS + 2H^+$
$2Cr^{3+} + 3H_2S \rightarrow Cr_2S_3 + 6H^+$	$Ni^{2+} + H_2S \rightarrow NiS + 2H^+$
Chromium sulphide is, in water, completely hydrolyzed to chromium hydroxide, according to the reaction:	$Pb^{2+} + H_2S \rightarrow PbS + 2H^+$ $HgCl_2 + H_2S \rightarrow Hg_3S_2Cl_2 + 2HCl$
$Cr_2S_3 + 6H_2O \rightarrow 2Cr(OH)_3 + 3H_2S$	$Hg_3S_2Cl_2 + H_2S \rightarrow 3HgS + 2HCl$

Notes: a] The compound $Hg_3S_2Cl_2$ can also be written as [HgCl2•2HgS]

b] The various iron sulphides have different colours: FeS2 (yellow); FeS (black, brown); Fe_2S_3 (yellow green) [CRC, Handbook of Chemistry and Physics (B-98)]

The iron ion (Fe^{2+}) does not produce any precipitation, in acid solution, with hydrogen sulphide[79]: because the concentration of the sulphide ion [S^{2-}] is insufficient. If the concentration of [H_3O^+] is reduced and that of the sulphide ion is increased with the addition of sodium acetate (CH_3COONa), there is a partial precipitation of iron sulphide FeS.

Note: The concentration of protons is reduced by the addition of sodium acetate (CH_3COONa) by hydrolysis[80]:

$$CH_3COO^- + H_3O^+ \rightarrow CH_3COOH + H_2O$$

The Hg^{2+} ion initially forms a white precipitate which, over time, becomes yellow, then brown and finally black; it is mercury sulphide. The white precipitate is the chlorine sulphide $Hg_3S_2Cl_2$ ($HgCl_2$•2HgS) (see the Hg^{2+} ration on page two (2).

PRODUCTION OF H_2S (g) AND ITS USE WITH SOLUTIONS OF METAL IONS

In this experiment, the precipitates of the metal sulphides described in tables 5 and 6 are obtained. In the system in figure 4 below, hydrogen chloride (HCl) frees hydrogen sulphide (H_2S) (g) from its ionic forms; nitrogen liberates H_2S(g) from the sulphurous water and transports it to the metal ion solution. A moistened lead acetate (ivory-white colour) paper is placed at the outlet of the flask containing the solution of the metal ion; it becomes dark grey: PbS (black) has been formed [81], according to the reaction:

$$Pb(OOCCH_3)_2(aq) + H_2S(g) \rightarrow PbS(s) + 2CH_3COOH(aq) \qquad [67]$$

The gaseous stream contains hydrogen sulphide. In another experiment, 10 drops of a 3% hydrogen peroxide (H_2O_2) solution are added to 20 mL of sulphurous water. The solution becomes yellowish in colour, then whitish and cloudy. The phenomenon can be interpreted by means of reactions:

$$H_2S(aq) + H_2O_2(aq) \rightarrow S(s) + 2H_2O(l) \qquad [68]$$

$$2H_2S(aq) + 5H_2O_2(aq) \rightarrow S(s) + H_2SO_4(aq) + 6H_2O(l) \qquad [69]$$

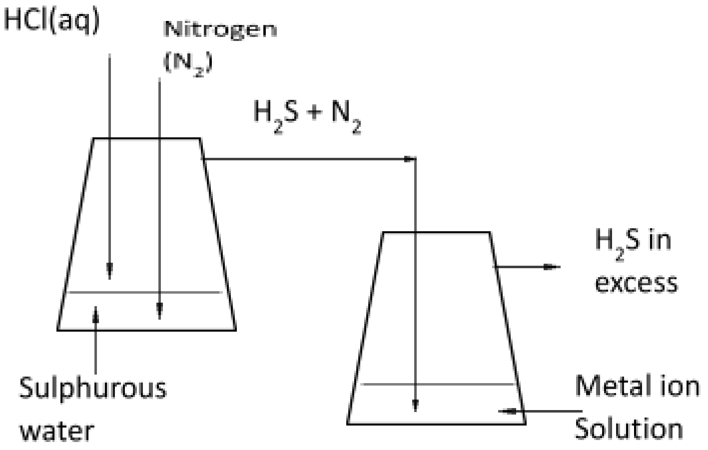
$$2H_2S(aq) + 4H_2O_2(aq) \rightarrow S(s) + SO_2 + 6H_2O(l) [70]$$

DIAGRAM OF THE H_2S (g) PRODUCTION AND UTILIZATION PLANT WITH METAL ION SOLUTIONS [Me^{n+}]

Figure 4

The containers are 250 mL flasks equipped with a pippio (gas outlet tube). In all experiments, the following solutions and their

Figure 4



The containers are 250 mL flasks equipped with a “pippio” (gas outlet tube). In all experiments, the following solutions and their respective quantities, are used.

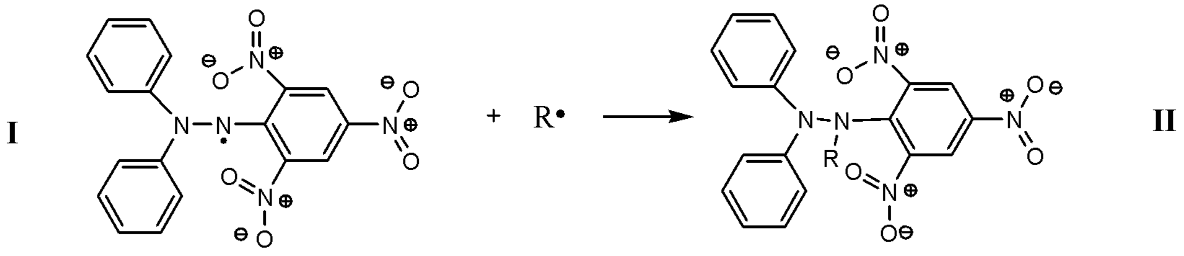
HCl (aq) concentration=6M; Volume of HCl=10 mL; Volume of Sulphurous Water=50 mL; Volume of the metal ion solution=50mL.; Concentration of metal ion =0.025 M.

The duration of bubbling is five minutes in all experiments.

DEMONSTRATION OF THE ABILITY OF HYDROGEN SULPHIDE (H_2S) TO INTERACT WITH FREE RADICALS AND BLOCK THEM

The stable radical DPPH (Diphenyl-Picril-Hydrazil)[82], structure I, is purple in colour and is used to study the ability of H_2S to interact with free radicals since DPPH is used as an "indicator" of radicals[83]. In a 100 mL beaker, 20 mL of deionized water is introduced; in another 100 mL beaker, 20 mL of sulphurous water is introduced. In each of the two beakers, add 30 drops of a solution of DPPH 10—4 M in acetone. Deionized water turns pale purplish pink; the sulphurous water turns light yellow and becomes cloudy.

REACTION 71

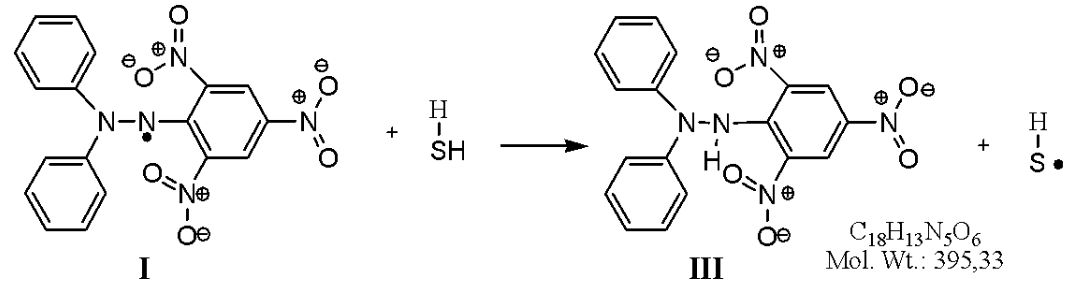


2,2-Difenil-1-picrilidrazile (DPPH) (cristalli violetti) $C_{18}H_{12}N_5O_6$ Mol. Wt.: 394,32

1,1-Difenil-2-picril- idrazina (sostituita)

It is also known that free radicals react rapidly with R–SH thiols[84], from which they easily extract the hydrogen atom; for this reason, H_2S can react with DPPH according to the reaction:

REACTION 72

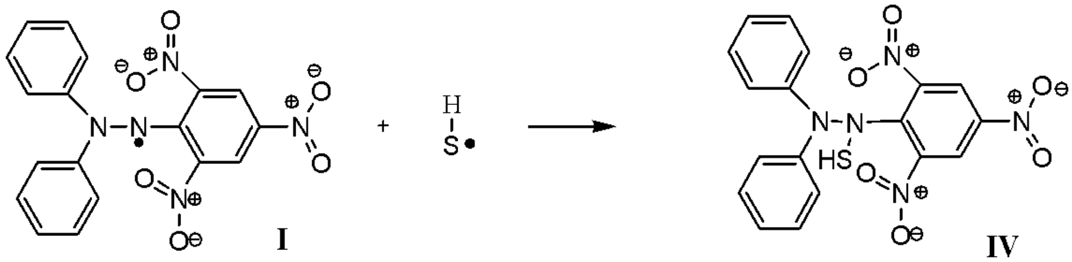


I

2,2-difenil-1-picrilidrazile (DPPH)

III

1,1-difenil-2-picrilidrazina (DPPHY)



I

IV

The purple DPPH behaves as an indicator of radicals with which it reacts by forming a molecule with paired electrons as in compounds II, III and IV which are coloured, clear or intensely yellow. The interpretation of the experiment is that in deionized water there is only a dilution effect; while in sulphurous water, H_2S behaves like a thiol (R–SH):

•DPPH + H_2S ▯ HDPPH + HS• [73]
•DPPH + HS• ▯ HS−DPPH [74]
•DPPH + HS• ▯ H−DPPH + S(s) [75]

The dot next to some molecules indicates an unpaired electron, that is, a radical. The release of elemental sulphur can be explained by the reaction [74] which accounts for the turbidity of the solution; while the disappearance of the radical •DPPH which turns into H−DPPH, which has a different colour, would explain the observed change in colour. This last experiment shows that H_2S can react with free radicals and block them, as DPPH is a free and stable radical.

CONCLUSIONS

Experimental research conducted on sulphurous water has shown that it can be used for those chemical applications where one of the compounds used is hydrogen sulphide: reduction reactions; precipitation of heavy metal ions as insoluble sulphides, to block free radicals; to recover sulphur. One of the most important is the recovery of elemental sulphur which could reduce its extraction from mines and/or its collection from the slopes of active volcanoes that are practiced in some parts of the world. Ultimately, sulphurous water has a certain versatility of use in very useful chemical processes that would justify its use as a raw material.

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