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Development of a Temperature Programmed Identification Technique to Characterize the Organic Sulphur Functional Groups in Coal

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Abstract: The Temperature Programmed Reduction (TPR) technique is employed for the characterisation of various organic sulphur functional groups in coal. The TPR technique is modified into the Temperature Programmed Identification technique to investigate whether this method can detect various functional groups corresponding to their reduction temperatures. Ollerton, Harworth, Silverdale, Prince of Wales coal and Mequinenza lignite were chosen for this study. High pressure oxydesulphurisation of the coal samples was also done. The characterization of various organic sulphur functional groups present in untreated and treated coal by the TPR method and later by the TPI method confirmed that these methods can identify the organic sulphur groups in coal and that the results based on total sulphur are comparable with those provided by standard analytical techniques. The analysis of the untreated and treated coal samples showed that the structural changes in the organic sulphur matrix due to a reaction can be determined.

Keywords: oxydesulphurisation; coal; characterization; organic sulphur

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1. Introduction

Sulphur in coal is classified into inorganic and organic sulphur. The inorganic part of sulphur includes disulphides and sulphates and is embedded in the coal while the organic part of sulphur is chemically bonded to the organic matrix of the coal. The different classes of sulphur compounds in coal can be quantitatively determined by standard methods [1]. Sulphate sulphur occurs in the form of calcium, iron and barium sulphates, but the amount is usually negligible. Almost all of the inorganic sulphur is present as the cubic pyrite or orthorhombic marcasite, whereas the organic sulphur may occur in different forms of functional groups like disulphides, aliphatic or aromatic thiols, aliphatic, aromatic or mixed sulphides and disulphides, heterocyclic compounds, thiophenes or condensed thiophenic structures [2–4]. Stable sulphur compounds can withstand severe decomposition reaction conditions [5,6], which makes it difficult to correlate analytical results of the coal products with an evaluation of the organic sulphur functional group distribution in the parent coal. The two main techniques for the quantification of organic sulphur groups are instrumental quantification and chemical quantification.

In the instrumental quantification the techniques that have proved most successful are all types of X-ray spectroscopy [4]. X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy can provide information on the chemical state of elements in solids and different functional groups but have certain limitations. Oxidation, pyrolysis and reduction are three chemical methods for the quantitative determination of organic sulphur functional groups [7]. LaCount et al. [8] investigated the controlled-atmosphere programmed-temperature oxidation (CAPTO) of coal. Calkins [9] proposed that the flash pyrolysis products from coal could be used to give an insight into the organic sulphur structures with some limitations. All the sulphur groups in coal could be converted to hydrogen sulphide by reducing solvents [10]. Each reduction reaction has a given activation energy and frequency factor which are different for different sulphur groups [11,12]. Majchrowicz [13,14] and Garcia [15] in their research also used a similar TPR procedure to characterise organic sulphur in Belgian and US coals.

There is one type of coal high organic sulphur content which has been extensively studied throughout Europe and the US, namely Mequinenza lignite, which can be used for comparison purposes. Using Mequinenza lignite, different researchers [16–21] used different techniques to study various organic sulphur groups. Table 1 shows the results of these studies.

Table 1. Mequinenza lignite results for various techniques.

Authors	Technique	Thiophenic %	Non-Thiophenic %
Torres-Ordoñez	Flash pyrolysis	33	67
Kelemen	XPS	34	66
Kelemen	XANES	48	52
Huffman	K-edge XANES	42	58
Majchrowicz	TPR	75	25
LaCount	CAPTO	64	36
Lafferty	TPR Hydrogenation	70	30

It can be seen that there is a wide variation in the thiophenic and non-thiophenic contents obtained by different methods for the same coal sample. In general the trends obtained for pyrolysis and the instrumental techniques are the same but totally different to that obtained for TPR and the oxidation method. Different limitations of the various techniques have also discussed elsewhere [4]. The coal samples have to be oxidised prior to analysis in order to distinguish between different groups. In addition to these problems the expensive experimental setup required, which includes a synchrotron in XANES and other X-ray equipment, limits the use of these techniques for routine analysis. It can be concluded that none of the investigations carried out so far can clearly explain the complex nature of coal matrix and each of the identification methods has its own limitations and more research is needed to get comparable results using a simple technique which is more amenable to routine analysis.

Simple and smaller molecules of organic sulphur present in coal break down producing hydrogen sulphide as a product gas quite easily with catalysed reducing agents under an increase in temperature. The behaviour of complex thiophenes towards the reducing conditions however limits the normal TPR analytical technique up to the identification of simple thiophenes, and thus the complex thiophenic part of organic sulphur is calculated by difference from the total organic sulphur content. This means that complex thiophenes are calculated and not determined. Another technique which has similarities to TPR is the so-called "Temperature Programmed Reduction" method [22]. The contribution of pyrite was also studied by partial float/sink removal and by HNO_3 extraction. However Meyers [23] explained that dilute warm nitric acid treatment of coal has been found to remove some organic sulphur by oxidation. Thus with a coal containing pyritic sulphur it is not possible to determine the exact organic sulphur species. In the case of a TPR analysis the pyrite interference is negligible, but complex thiophenes have to be calculated by difference.

In view of the limitations of both the techniques an attempt has been made to modify the TPR method by combining both the techniques one after the other during an experimental run for the characterisation of all the sulphur species in coal. The resulting method has been named Temperature Programmed Identification (TPI).

2. Experimental

2.1. Principle of Temperature Programmed Reduction

Several researchers [10,24] have described the fundamental theory of the TPR method. Mathematical equations for the rate of evolution of a gas from a sample as a function of the temperature during pyrolysis experiments with a linear temperature-time program can be found in [16,25,26] listed in Table 2. According to these equations, if it assumed that each group can be reduced to H_2S by a first order reaction. Then considering the reduction of the aliphatic sulphide, we have:

$$\frac{d[H_2S]}{dt} = k_1[R\text{–}S\text{–}R'] \tag{1}$$

The index 1 is used to denote the sulphidic functional group; R–S–R′. If it is also assumed that the rate constant k_1, depends on temperature, then, according to the Arrhenius equation:

$$k_1 = A_1 e^{-\frac{E_{a1}}{RT}} \tag{2}$$

where A_1 is the frequency factor and E_{a1} the activation energy for the reduction. Substituting the value of k_1 from Equation (2) into Equation (1):

$$\frac{d[H_2S]_1}{dt} = A_1 e^{-\frac{Ea1}{RT}}[R\text{–}S\text{–}R'] \tag{3}$$

The rate constant of the reduction becomes larger at higher temperatures which means that the rate of depletion of sulphide becomes larger at higher temperatures. The rate of evolution of H_2S from a sample with a fixed amount of the sulphide with increasing temperature will increase initially due to this increase in temperature, but since the concentration of the sulphur is depleted in the process, due to the evolution of H_2S, the rate will then fall. The mathematical equation which describes the rate of evolution of gas as a function of the temperature of the sample, where the temperature is increased linearly with time, postulates that, the temperature of the sample is increased according to the equation given below:

$$T = T_0 + \alpha\, t \tag{4}$$

where T_0 is the initial temperature (K), α is the rate of heating, K/min, and t is the time, (min.).

Then the volume of H_2S, V_i, that evolves when the i-th group is reduced, follows the equation:

$$\frac{dVi}{dt} = \frac{dT}{dt}\frac{A_i V_{i\infty}}{\alpha}\exp[-\frac{E_i}{RT} + \frac{A_i RT^2}{E_i}(1 - \frac{2RT}{E_i})e^{-\frac{E_i}{RT}}] \tag{5}$$

where T is sample temperature (K) and $V_{i\infty}$ denotes the total volume of H_2S that will evolve as a result of complete reduction of the i-th group. The temperature at which the rate of evolution of H_2S from the i-th group reaches its maximum is denoted by T_{mi}, and is unique function of E_{ai} and A_i and the rate of heating, α:

$$\frac{RT_{mi}^2 A_i}{\alpha E_{ai}} = e^{-\frac{E_{ai}}{RT_{mi}}} \tag{6}$$

Equation (6) means that if the sample is heated at the constant rate α, the apex of the H_2S peak from the i-th group which is reduced has different parameters, E_{aj} and A_j. When a mixture which contains several functional groups is reduced, the behaviour of each group is similar, except that each peak will appear at different T_m.

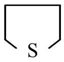
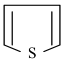
2.2. Experimental Equipment

The experimental apparatus consisted of a tube furnace and a gas chromatograph. The coal samples were prepared and placed in the tube furnace in a ceramic boat. The tube furnace was heated at a specified rate. The downstream end of the tube furnace was connected to a Perkin Elmer-gas chromatograph, by a stainless steel tube of 3 mm diameter. The hydrogen sulphide gas produced by the reduction of the organic sulphur functional groups present in the coal sample was carried to the chromatograph by a continuous flow of nitrogen through the tube furnace. This nitrogen-H_2S mixture was automatically injected into the chromatograph by a computer programmed pneumatic gas sampling valve.

2.3. Sample Preparation and Operating Conditions

The coal samples were ground (<51 µm) to reduce the effect of mass transfer. The ground samples were pre-extracted with 5% *v*/*v* HCl to remove carbonates as soluble chlorides [27,28]. The relatively fine particle size assisted reagent penetration and minimised the retention of evolved H_2S. Acid washing dissolved the alkaline minerals which could react with evolved H_2S, and regenerated any thiols bound as calcium thiolates. Coal (40–500 mg, according to the organic sulphur content) was impregnated with pyrogallol, the principle reducing agent. Pyrogallol (250 mg) was added as a 50% *w*/*v* solution in methanol. The solvent was allowed to evaporate. The dried coal was then slurried with tetralin (1,2,3,4-tetrahydronaphthalene). Six to eight drops or 200 mg of tetralin was used. 9,10-Dihydrophenanthrene (125 mg) and resorcinol (100 mg) were also added to this slurry. Finally 1 to 2 mg of sulphidised cobalt-molybdenum catalyst (Harshaw 0402) was added to enhance the rate of reduction of the sulphur groups. After preparation the samples were left overnight in the ceramic boat for better impregnation of the reducing chemicals. The tube furnace was heated at a predetermined rate (typically 2–5 °C/min) from room temperature to 600 °C with a nitrogen flow of 20 mL/min. A Chromosil 330 column was selected as it is ideally suited for all types of Sulphur-containing gases [29]. The concentrations of mercaptans, RSH and thiophenes can accurately be determined in the finely ground (<51 µm) coals [27,30].

Table 2. Reduction temperatures for organic sulphur groups.

Model Compounds/Group	**Structure**	**Model Compounds Reduction Temperature °C**	**Coal Temperature °C**
Disulphide/Elem. Sulphur	-S-S	<160	20–120
Mercaptans	R-SH	160–210	140–220
Aryl Thiols	Ar-SH	200–240	220–280
Aliphatic Sulphides	R-S-R	270–330	270–350
Alicyclic Sulphides		320–360	340–390
Aryl Sulphides	Ar-S-R	450–470	390–530
Thiophenes (simple)		500–600	520–600

The amount of H_2S evolved from a particular organic sulphur functional group was determined by mathematical integration as follows;

$$A = \frac{\sum \text{of the ppm of a functional group/No. of peaks of that group}}{10^6} \quad (7)$$

$$B\ (\text{mL}) = A \times \text{Nitrogen flow}\ (20\ \text{mL/min}) \times \text{Total time for that group to elucidate (min)} \quad (8)$$

$$\text{C (g) of sulphur in a particular group} = \text{B (mL)} \times \text{Density of } H_2S \text{ (0.00152 g/mL)} \times \text{0.9412 (g of sulphur/g of } H_2S) \quad (9)$$

2.4. Experimental Runs with Modification of the TPR

The temperature programmed experimental runs were performed on the different coal samples, namely: Ollerton, Harworth, Silverdale and Prince of Wales. Untreated and representative oxydesulphurised samples were run in order to check and identify the structural changes incorporated to the coal matrix due to particular oxydesulphurisation reaction. The temperature ramp rate between the range of a particular group was kept between 2–5 °C. Analysis of the coals used in this study are given in Table 3 on an "as received basis".

Table 3. Sulphur analysis of the samples for TPR study.

Sample	S_T	S_P %	S_S %	S_O %	Ash %
Ollerton	1.50	1.19	0.04	0.27	41.00
Harworth(U.T)	2.31	1.54	0.03	0.74	49.64
Harworth(T)	1.29	0.77	0.01	0.51	49.34
Silverdale(U.T)	5.31	4.23	0.03	1.05	30.54
Silverdale(T)	3.34	2.41	0.01	0.92	29.39
POW(U.T)	2.22	1.10	0.09	1.03	13.03
POW(T)1	0.68	0.05	0.01	0.62	11.43
POW(T)2	0.69	0.04	0.04	0.61	10.69

(U.T) = Untreated, (T) = Treated.

For the Temperature Programmed Identification (TPI) technique, the experimental run is split into two parts, i.e., normal Temperature Programmed Reduction (TPR) analysis and normal Temperature Programmed Oxidation (TPO) analysis in a sequence of TPO after TPR.

During the 1st part, using normal TPR analysis, identification of all the organosulphur species up to simple thiophenes. The simple thiophenes emit H_2S between 520–600 °C. After complete evolution of H_2S from simple thiophenes the furnace was cooled down to <200 °C. Then the 2nd part of the analytical run was started. It should be noted that at this stage there are only three main groups left behind i.e., pyrite, complex thiophenes and inorganic sulphates. The oxidation temperature ranges as found by [16–22] for the evolution of SO_2 for these three groups are pyrite (250–380 °C), complex thiophenes (450–600 °C), and inorganic sulphates (above 650 °C), respectively.

3. Results and Discussions

3.1. Samples Analysed by Temperature Programmed Reduction

3.1.1. TPR of Ollerton Coal

The organic sulphur content of the coal was 0.27%. The results of the detected functional groups were calculated from the data values of the chromatographic traces. These results are given in Table 4.

Table 4. Results for the TPR of untreated ollerton coal.

Functional Group	Temp. Range (°C)	Sulphur Recovered (g)	% of S_O
Disul./Elem. Sulphur	20–120	-	-
Mercaptans	140–220	-	-
Aryl Thiols	220–280	6.21×10^{-6}	0.73
Aliphatic Sulphides	270–350	2.60×10^{-5}	3.06
Alicyclic Sulphides	340–390	3.94×10^{-5}	4.64
Aryl Sulphides	390–530	1.05×10^{-4}	12.37
Simple Thiophenes	520–600	1.93×10^{-4}	22.73
Complex Thiophenes	Above 600	4.79×10^{-4}	56.47

It can be seen from the results that nearly 80% of the organic sulphur present in the Ollerton coal sample is in the form of thiophenes, out of which around 57% is complex. Apart from thiophenes aryl sulphides are also present in reasonable amounts. The rest of the functional groups were present in very small amounts. The chromatographic trace is given in Figure 1.

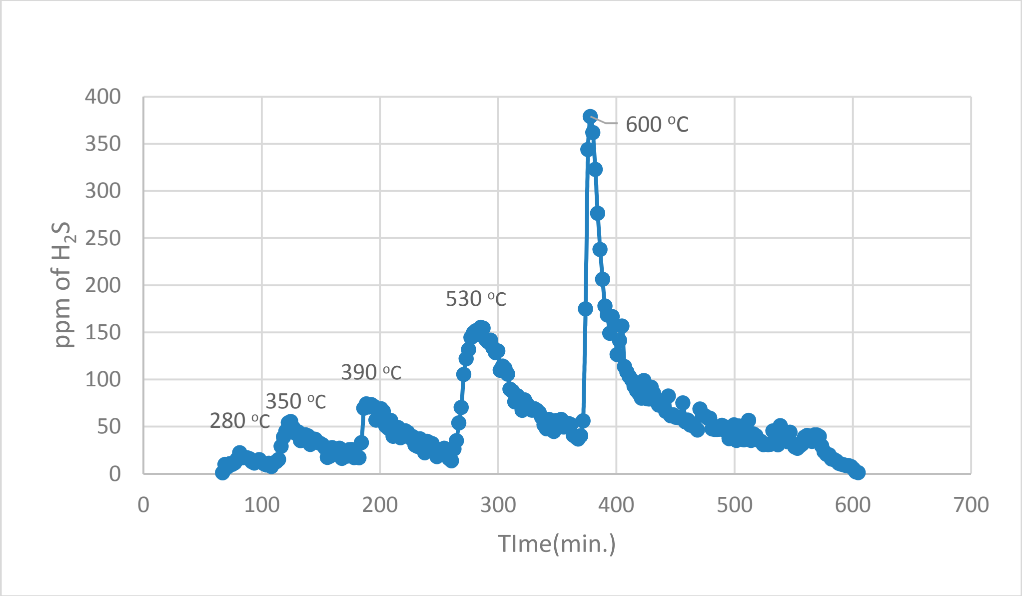


Figure 1. TPR of untreated ollerton coal.

3.1.2. TPR of Harworth Coal

The organic sulphur content of this untreated coal was 0.74%. Treated coal used in this run was a sample which was previously oxidised for one hour under 300 bar of air pressure at 100 °C with a coal slurry concentration of 5%. The organic sulphur content of this treated coal was 0.51%. The results of this experimental run are given in Table 5.

Table 5. Results for the TPR of treated and untreated harworth coal.

Functional Group	Temp. Range (°C)	% of S_O Untreated Coal	% of S_O Treated Coal
Disul./Elem. Sulphur	20–120	0.43	0.51
Mercaptans	140–220	0.47	6.26
Aryl Thiols	220–280	0.94	2.17
Aliphatic Sulphides	270–350	1.31	6.73
Alicyclic Sulphides	340–390	9.44	6.54
Aryl Sulphides	390–530	29.05	17.00
Simple Thiophenes	520–600	31.01	31.67
Complex Thiophenes	Above 600	27.35	29.12

It can be seen from the results that around 58% of the organic sulphur present in the Harworth coal is in the form of thiophenes, out of which 27% is complex and 31% simple. Apart from thiophenes aryl sulphides are also present in reasonably high amounts. The rest of the groups present were comparatively in very small amounts. Figure 2 shows the chromatographic trace for this run.

From the results given in Table 5 for treated Harworth coal, it can be seen that on the overall basis the total thiophenic content of the treated coal was unaffected by the oxidation reaction. However there was a significant breakdown of aryl sulphide groups. The alicyclic sulphides group was also affected by the oxidation reaction and treatment resulted in around 31% of its removal.

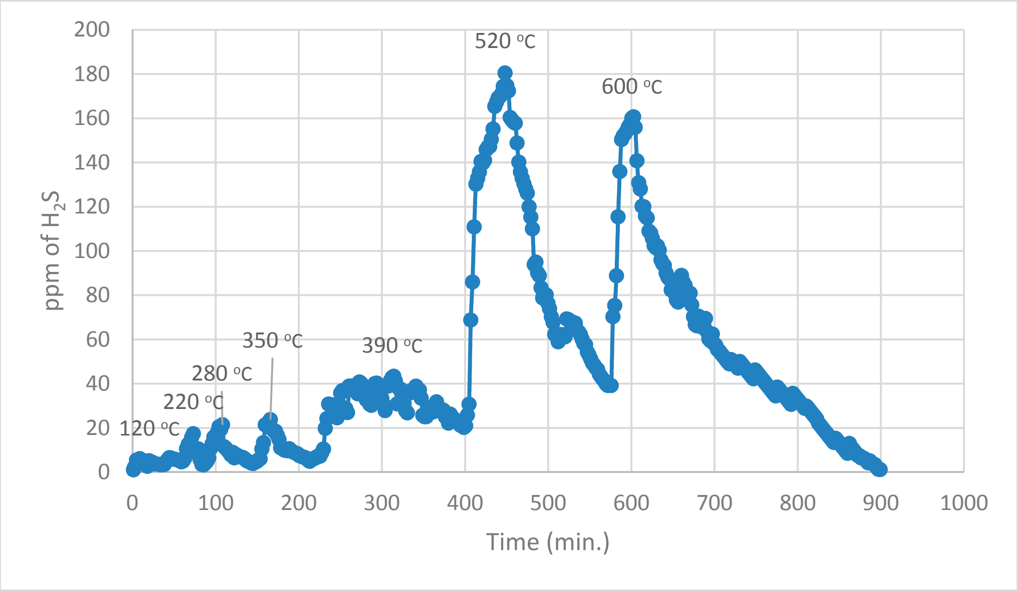


Figure 2. TPR of untreated harworth coal.

As a result of this breakdown of these groups some lower functional groups were made, which can be seen by the increased percentages of mainly aliphatic sulphides, aryl thiols and mercaptans. Figure 3 shows the chromatographic trace.

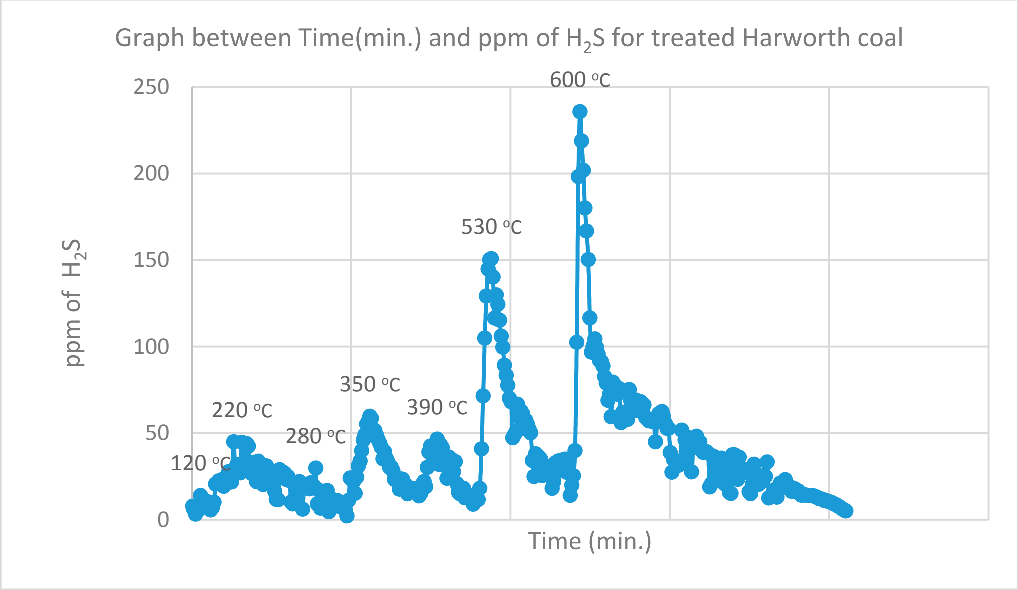


Figure 3. TPR of treated harworth coal.

3.1.3. TPR of Silverdale Coal

The organic sulphur content of the untreated coal was 1.05%. The treated coal used in this run was previously oxidised at 150 °C and 300 bar for one hour with a coal slurry concentration of 5%. The organic sulphur content of treated coal was 1.30%. The results of the run are given in Table 6, while the chromatographic trace is shown in Figure 4. From the results it can be seen that the thiophenic content, comprising both simple and complex thiophenes, of the untreated sample is around 84%, while all the other groups present are in very small amounts.

Table 6. Results for the TPR of Silverdale Coal.

Functional Group	Temp. Range (°C)	% of S_O Untreated Coal	% of S_O Treated Coal
Disul./Elem. Sulphur	20–120	0.45	0.13
Mercaptans	140–220	2.65	7.83
Aryl Thiols	220–280	1.02	8.20
Aliphatic Sulphides	270–350	3.68	10.25
Alicyclic Sulphides	340–390	2.48	5.51
Aryl Sulphides	390–530	5.75	4.47
Simple Thiophenes	520–600	27.60	3.60
Complex Thiophenes	Above 600	56.37	60.01

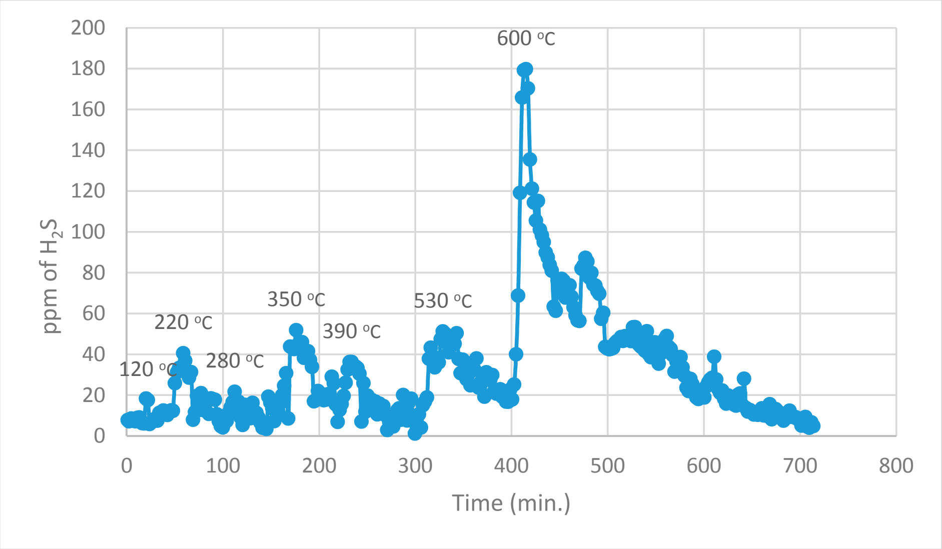


Figure 4. TPR of untreated silverdale coal.

From the results given in Table 6 for treated Silverdale coal, it can be seen that the simple thiophenic content has broken down into the other non-thiophenic groups due to the oxidation reaction, while the complex thiophenes were unaffected. As a result of the oxidation reaction some organic sulphur was removed. This structural breakdown and removal also resulted in a percentage increase of the non-thiophenic groups. Figure 5 shows the chromatographic trace.

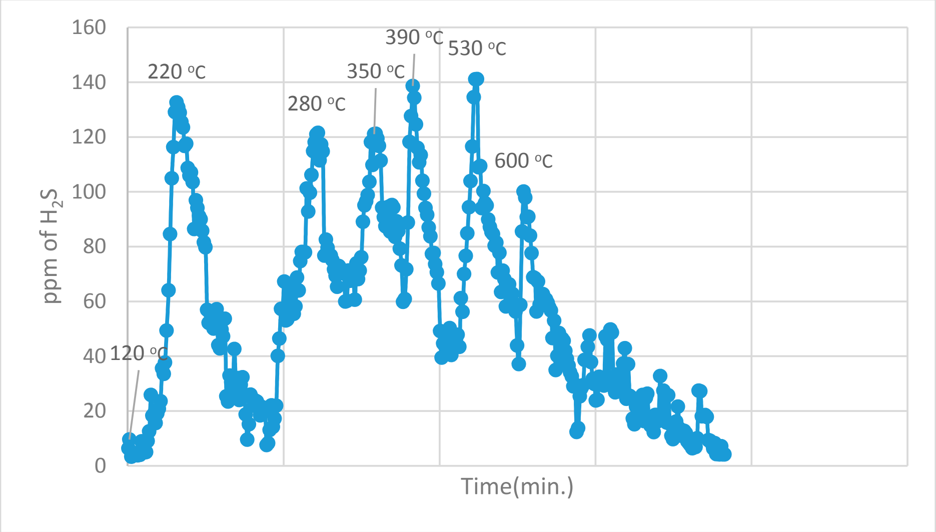


Figure 5. TPR of treated silverdale coal.

3.1.4. TPR of Prince of Wales

The organic sulphur content of the untreated coal was 1.03%. Treated coal sample POW1 is that of a coal sample which was treated with 10% *w*/*v* potassium permanganate solution under 300 bar air pressure, 25 °C temperature for one hour. Treated coal sample POW2 is that of a coal sample which was treated for one hour with 10% *w*/*v* potassium permanganate solution prepared in 20% *v*/*v* acetone under atmospheric pressure and 25 °C. The organic sulphur content of the POW1 and POW2 coal samples was 0.62% and 0.61%, respectively. More details about oxydesulphurisation can be read elsewhere [31].

Figure 6 shows the chromatographic trace of the untreated POW coal. From the results it can be seen that organic sulphur is distributed quite uniformly in four functional groups. The highest being the alicyclic sulphides having around 25% of the organic sulphur. Apart from alicyclic sulphides the next dominating group detected was simple thiophenes having about 23% of the organic sulphur. On the overall basis the thiophenic and non-thiophenic groups were approximately 50% of the organic sulphur. Table 7 shows the results of this run.

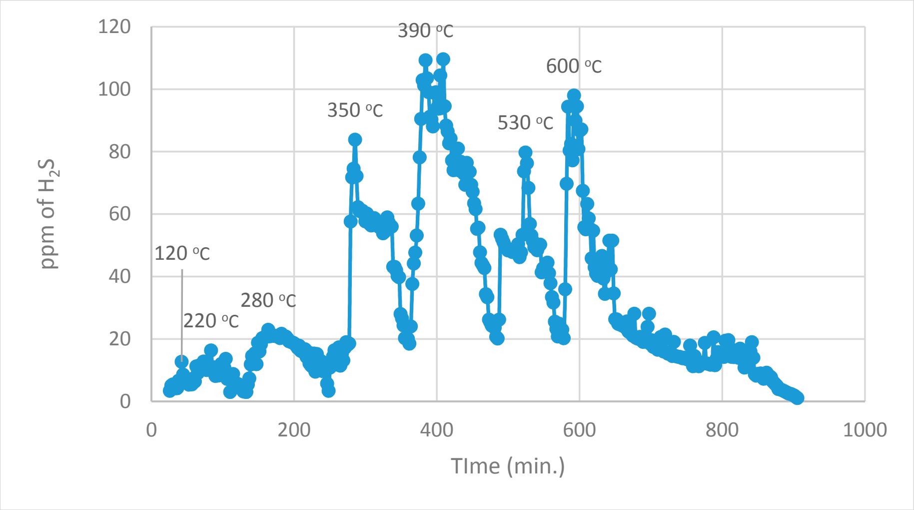


Figure 6. TPR of untreated POW coal.

Table 7. Results for the TPR of untreated and treated prince of wales coal.

Functional Group	Temp. Range (°C)	% of S_O Untreated POW Coal	% of S_O Treated POW1 Coal	% of S_O Treated POW2 Coal
Disul./Elem. Sulphur	20–120	-	1.25	0.16
Mercaptans	140–220	2.51	0.73	16.24
Aryl Thiols	220–280	5.47	1.24	22.05
Aliphatic Sulphides	270–350	13.94	13.00	7.35
Alicyclic Sulphides	340–390	25.01	16.06	1.22
Aryl Sulphides	390–530	12.40	15.90	1.74
Simple Thiophenes	520–600	22.65	9.60	1.65
Complex Thiophenes	Above 600	17.75	42.22	49.59

From the results it can be observed that a similar trend as was observed in the previous cases of treated Harworth and Silverdale coal samples is also followed by treated POW1 coal, i.e., the reduction in the simple thiophenes. Since potassium permanganate is a very strong oxidising agent it resulted in not only the breakdown of the bigger molecules but it also removed a significant amount of various groups. There was only an increase observed in the case of aryl sulphides amount while all the other families experienced a decrease in their amounts. It should be noted that in the untreated analysis there was no disulphide/elemental sulphur group present, since most of the mercaptans were removed, it is probable that the elemental sulphur formation took place during the oxydesulphurisation reaction. Figure 7 shows the chromatographic trace of the run.

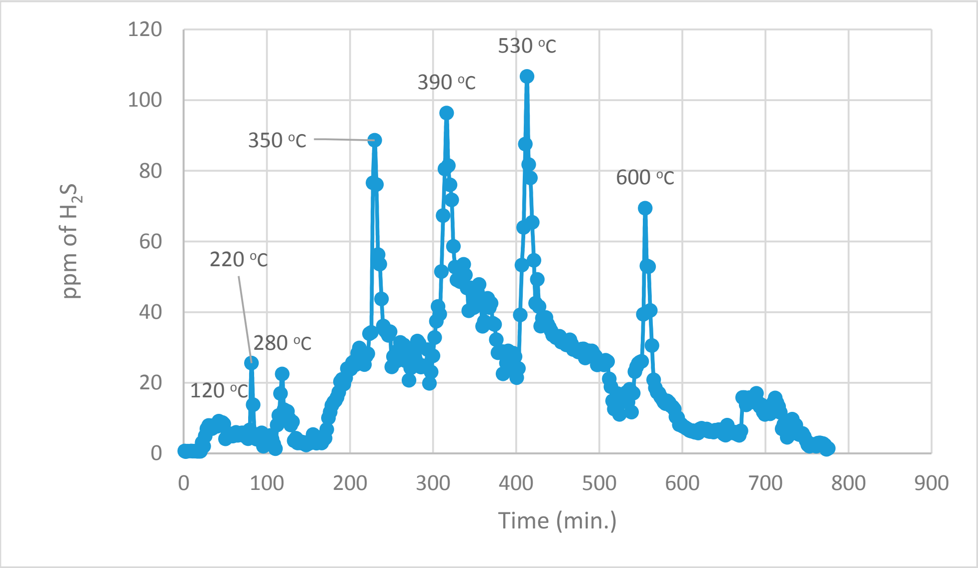


Figure 7. TPR of treated POW1 coal.

Figure 8 shows the chromatographic trace for treated POW2 coal. It can be seen from the results that the similar trend as observed in the previous cases of treated coals is valid in this case as well. In addition to the breakdown behaviour of simple thiophenes, acetone removed the major part of the oxidised sulphur species, however this breaking down of simple thiophenes resulted in the increase of the aryl thiol and mercaptan groups amounts. Disulphides/elemental sulphur group formation was negligibly small. The reason for this could be that either in the presence of acetone no elemental sulphur formation took place, or during the breakdown process of the larger molecular weight compounds acetone dissolved the major intermediates preventing any further breakdown. The evidence to support this statement was observed in carrying out experiment where almost all volatiles were extracted by acetone during the first filtration stage after experiment and dried coal was composed of a powder-like product.

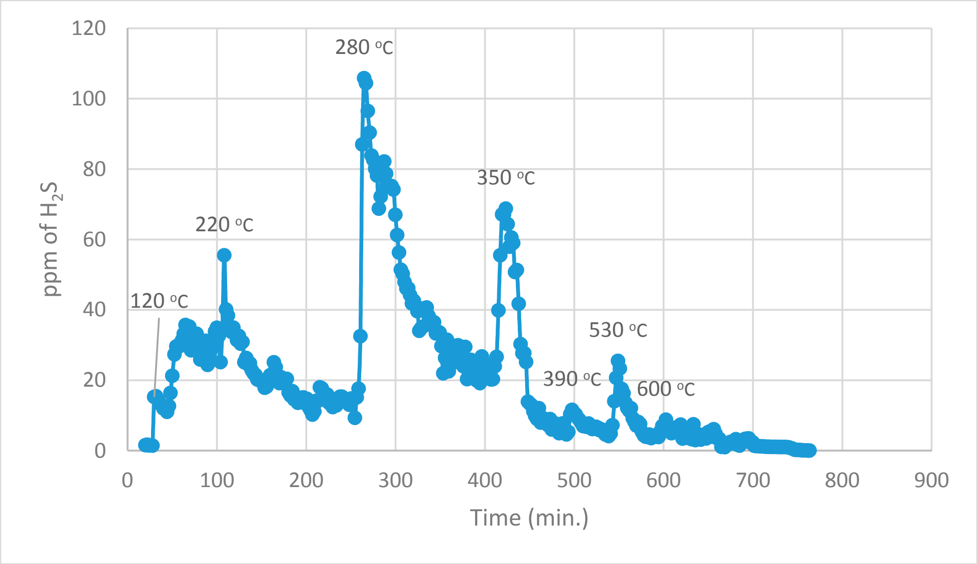


Figure 8. TPR of treated POW2 coal.

3.1.5. Overall Discussion

All the results gave reasonably distinct groups. The result of Ollerton untreated coal gave a reasonably good understanding of the working of the TPR method. Similar groups were observed by Zhang et al. [7]. The results of the untreated and treated Harworth coal gave an explanation of the behaviour of organic sulphur species towards the oxydesulphurisation reactions via a major breakdown of aryl sulphide groups. The reaction conditions at 100 °C temperature and 300 bar pressure did not have any effect upon the thiophenic content of the coal. However, all the lower functional groups were affected. This meant that the reaction conditions did not oxidise the thiophenes.

The runs that were performed on the untreated and treated Silverdale coal showed similar results. The higher temperature (150 °C) in addition to the groups up to aryl sulphides also broke down simple thiophenes. As a result of this breakdown some of the organic sulphur was removed, however the complex thiophenic part of the thiophenes was not affected even at 150 °C. Thus on the overall basis the complex thiophenes were increased by 4%. The high complex thiophenic content of Silverdale coal also explains why the organic sulphur removal was lower in air oxydesulphurisation reactions as compared to Prince of Wales and Harworth coals.

The runs that were performed on the treated and untreated Prince of Wales coal samples again confirmed the behaviour of sulphur species towards oxydesulphurisation. The use of a strong ambient temperature oxidant like potassium permanganate incorporated more structural changes than was observed at 150 °C in the previous case of Silverdale coal. The runs performed on POW1 resulted in quite a major breakdown and removal of all the families up to the simple thiophenes. Complex thiophenes however remained unaffected. The runs performed on POW2 also gave similar results. It should be noted that coal is mainly insoluble in acetone. However, volatile material present in coal, being composed of relatively very small molecular structures, can be extracted by this solvent. Since the oxydesulphurisation reactions breaks down the higher molecular weight molecules the acetone extracted most of the broken down species along with all the volatiles [32]. Since the complex thiophenes did not participate in reaction thus on the overall basis the percentage of the complex thiophenes was increased.

3.2. Samples Analysed by Temperature Programmed Identification (TPI) Technique

The TPI runs were performed on two representative coal samples. These coal samples were Prince of Wales and Mequinenza lignite, of which only Prince of Wales was run on both untreated and oxydesulphurised form. The Mequinenza lignite was investigated to compare the results with other researchers since it is the only coal investigated by most of researchers. A TPI analysis was also performed on pure iron pyrite mineral. The reason for doing this run was to check the accuracy of the analysis, to confirm that pyritic sulphur does not interfere with the analysis and to find the exact temperature range for the elucidation of SO_2 from the mineral. The analysis of the coals and mineral pyrite are presented in Table 8 on an "as such" basis. The analysis of the acid washed pyrite mineral was performed according to the method of mixed acids.

Table 8. Sulphur Analysis of the Samples for TPI Study.

Sample	S_T %	S_P %	S_S %	S_O %	Ash %
Iron Pyrite	53.33	53.33	-	-	-
Prince of Wales (U.T)	2.209	1.096	0.087	1.026	13.03
Prince of Wales (T)	0.399	0.010	0.001	0.388	12.01
Mequinenza Lignite	9.560	1.390	0.151	8.020	14.48

3.2.1. TPI of Iron Pyrite

The amount of mineral pyrite taken for the analysis was 0.0019 g. Total sulphur recovered as $H_2S + SO_2$ was 9.6054×10^{-4} g.

The chromatographic trace is presented in Figure 9. The results calculated from the data values are reported in Table 9. From the results it can be seen that a very small amount of H_2S was evolved from the pyrite mineral in the range of 270–350 °C which is the temperature range for aliphatic sulphides. The reason for this as explained earlier is the formation of a metallic iron layer over the surface of the mineral that stopped any further evolution of H_2S. During the 2nd part the elucidation of SO_2 started at 230 °C and the increase in temperature was stopped at 380 °C at which all the rest of the pyrite produced SO_2 by reacting with oxygen passing as carrier and oxidising agent through the tube furnace

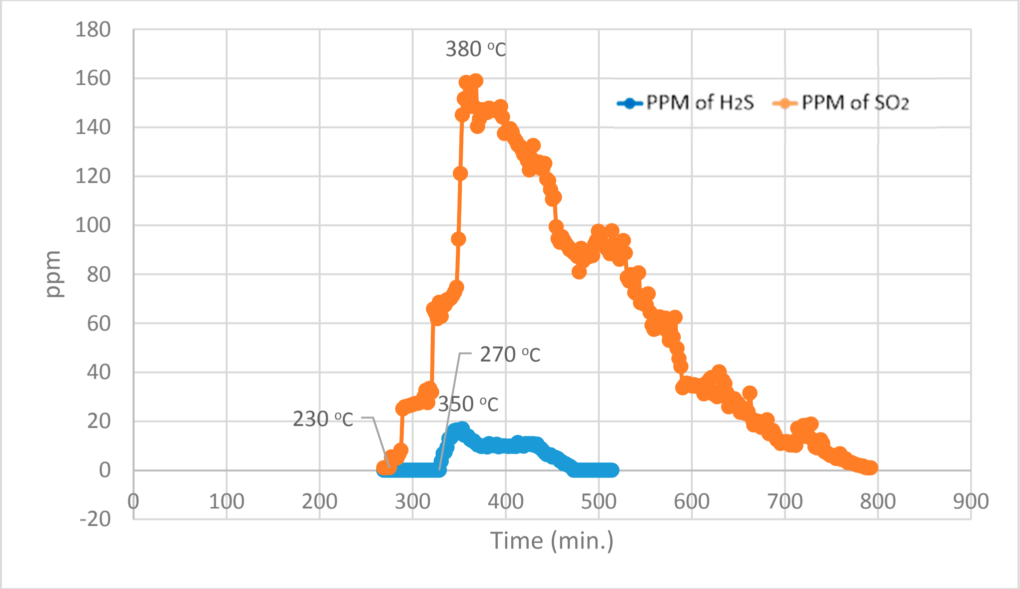


Figure 9. TPI of iron pyrite.

Table 9. Results for the TPI of iron pyrite.

Functional Group	**As**	**Temp. Range (°C)**	**Sulphur Recovered (g)**	**% of S Recovered**
Aliphatic Sulphides	H_2S	270–350	1.8405×10^{-5}	1.91
Pyrite	SO_2	230–380	9.4214×10^{-4}	98.09

3.2.2. TPI of Prince of Wales Coal

The amount of the coal sample taken for the TPI analysis was 0.1578 g. The organic sulphur content of the untreated and treated coal was 1.026% and 0.388% respectively, while the pyritic sulphur content was of 1.096%. Coal samples were treated with 10% w/v solution of potassium permanganate prepared in 4% w/v solution of potassium hydroxide for one hour under 300 bar air pressure. The temperature of the system was 25 °C, while the coal slurry concentration was 5%.

The results of the TPI runs for untreated and treated POW coal are presented in Table 10. From the results for untreated coal, it can be seen that over 90% of the pyritic sulphur taken was recovered as sulphur dioxide. On the overall organic sulphur is distributed 50% as thiophenic and 50% as non thiophenic. Alicyclic sulphides group is the major among the non-thiophenic part, while simple thiophenes group is next to alicyclic sulphides and more than complex thiophenes group. Chromatographic trace for untreated POW coal is shown in Figure 10.

Table 10. Results for the TPI of untreated prince of wales.

Functional Group	**Recovered** As	**Temp. Range** (°C)	**% of S_O** for untreated POW coal	**% of S_O** for treated POW coal
Disul./Elem. Sulphur	H_2S	20–120	-	-
Mercaptans	H_2S	140–220	2.51	
Aryl Thiols	H_2S	220–280	5.46	
Aliphatic Sulphides	H_2S	270–350	13.91	7.87
Alicyclic Sulphides	H_2S	340–390	24.95	12.33
Aryl Sulphides	H_2S	390–530	12.37	13.65
Simple Thiophenes	H_2S	520–600	22.60	14.90
Pyrite	SO_2	230–380	-	-
Complex Thiophenes	SO_2	600	18.20	51.25

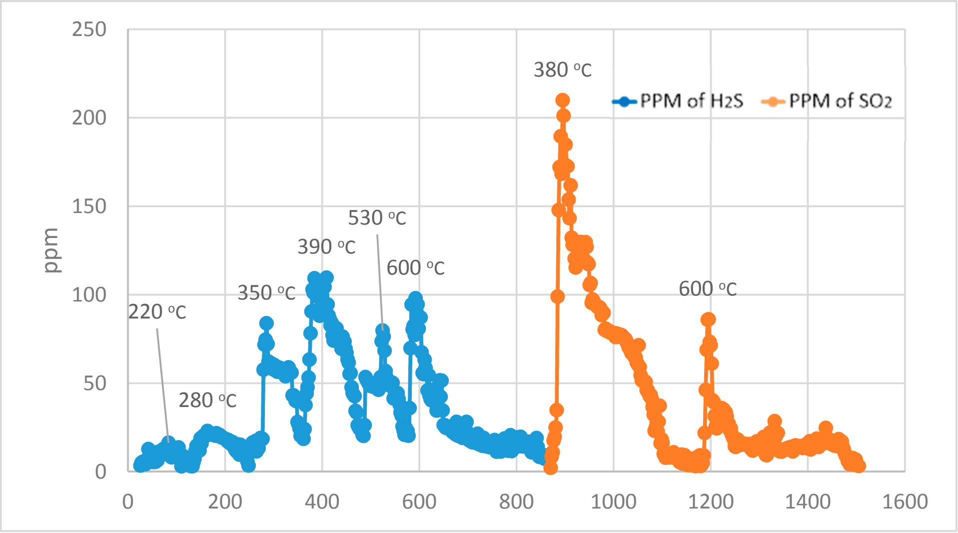


Figure 10. TPI of untreated POW coal.

For treated POW coal it can be seen from the results that most of the non-thiophenic part and about 34% of simple thiophenes have been removed. The largest group left behind is composed of complex thiophenes. About 90% pyritic sulphur was recovered as SO_2.

The first three groups were completely removed by the oxydesulphurisation reaction conditions, while the rest of the groups with the exception of complex thiophenes also showed substantial removal. Figure 11 shows the chromatographic trace for the treated POW coal.

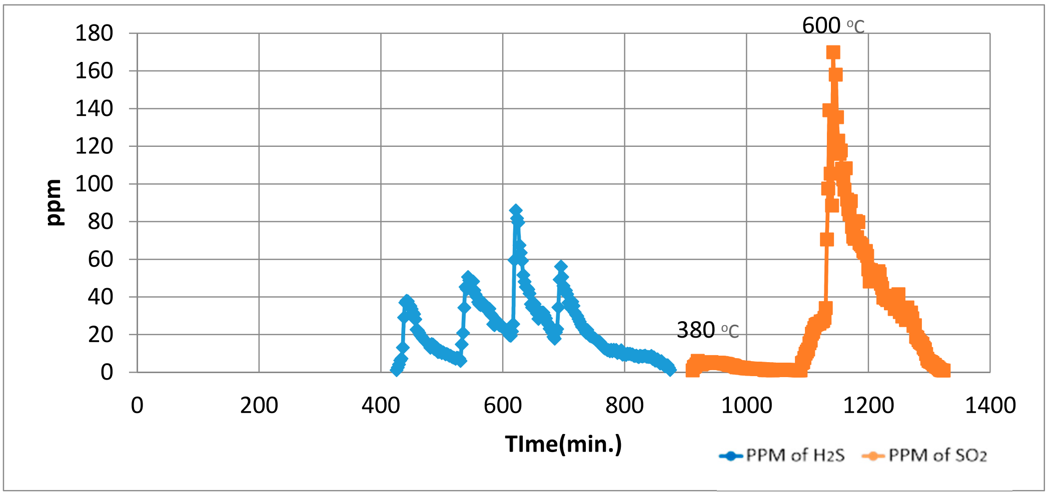


Figure 11. TPI of treated POW coal.

3.2.3. TPI of Mequinenza Lignite

0.0552 g of the acid washed coal was taken for the analysis. The amount of organic sulphur in coal was 8.020% and amount of pyritic sulphur was 1.390%. The results of the TPI analysis are shown in Table 11. From the results it can be seen that about 20% of organic sulphur in this coal is present as thiophenes, while 80% as non-thiophenic. Functional groups with highest/significant composition are alicyclic sulphides followed by aryl sulphides Simple thiophenes are present and they are the dominant part of thiophenes. Figure 12 shows the chromatographic trace for the analysis

Table 11. Results for the TPI of mequinenza lignite.

Functional Group	Recovered as	Temp. Range (°C)	Sulphur Recovered (g)	% of S_O Recovered
Disul./Elem. Sulphur	H_2S	20–120	1.443×10^{-5}	0.33
Mercaptans	H_2S	140–220	4.014×10^{-4}	9.07
Aryl Thiols	H_2S	220–280	3.401×10^{-4}	7.69
Aliphatic Sulphides	H_2S	270–350	8.231×10^{-4}	18.61
Alicyclic Sulphides	H_2S	340–390	1.009×10^{-3}	22.81
Aryl Sulphides	H_2S	390–530	9.678×10^{-4}	21.88
Simple Thiophenes	H_2S	520–600	7.655×10^{-4}	17.36
Pyrite	SO_2	230–380	6.982×10^{-4}	-
Complex Thiophenes	SO_2	450–600	1.011×10^{-4}	2.25

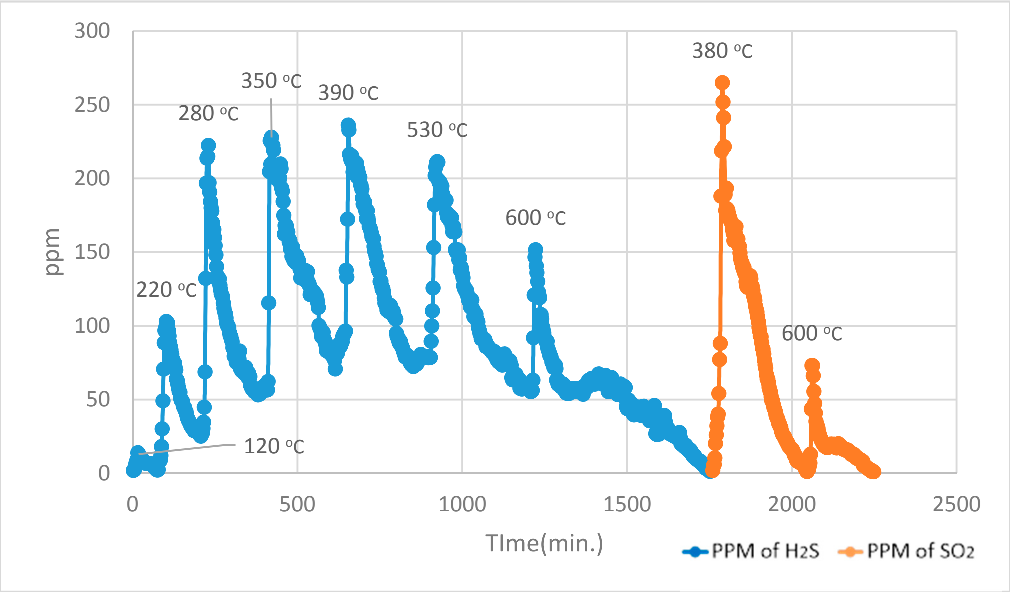


Figure 12. TPI of untreated mequinenza lignite.

3.2.4. Discussion of Results

The TPR results on iron pyrite confirmed the findings of previous researchers [33]. The amount elucidated was detected in the temperature range of aliphatic sulphides. The little H_2S evolution seemed to confirm the postulation that metallic iron layer formation on the surface of pyrite prevents diffusion of the reducing species. The production of SO_2 during the second half of the TPI run also confirmed the findings of previous researchers [33]. All the remaining sulphur was recovered as SO_2. The start of SO_2 evolution at 230 °C which is 20 °C less than the temperature reported by previous researchers [33] could be due to the reason that no diluting agent like WO_3 was used. The production of SO_2 from iron pyrite in a temperature range far away from the thiophenic oxidation temperature further supported the idea that both pyritic and thiophenic sulphur species could be identified.

The results of the runs that were performed on untreated and treated Prince of Wales coal samples indicated quite a clear effect of the oxydesulphurisation reactions on coal structure and were similar to the TPR results. The oxidation of sulphur species with alkaline potassium permanganate brought about some structural changes in the organic sulphur functional groups present in the coal. Major changes were the breaking down of simple thiophenes and aryl sulphides resulting in their removal from coal. It should be noted that during the previous TPR work the run performed on a treated sample of Prince of Wales coal with normal 10% w/v potassium permanganate under 300 bar the non-removal of aryl sulphides was reported, while alkaline potassium permanganate effected the removal of aryl sulphides. It was observed that alkaline potassium permanganate is a stronger oxidising agent than potassium permanganate alone. The TPI findings for the untreated Mequinenza lignite validated those obtained by flash pyrolysis [9], XPS [17,18], and K-edge XANES [19], respectively.

4. Conclusions

The use of the TPI technique is quite straightforward and the mixing of different groups is negligible. The results on the basis of overall recovery are comparable with those obtained by the standard analytical techniques. The very slight difference could be due to the reason that the detection device in the case of the gas chromatograph is very sensitive. Above all the TPI technique is quite simple as it does not involve the use of very expensive and special machines like X-rays and synchrotrons, etc. Due to the non-availability of such equipment TPI can be used as a routine laboratory analysis technique for the complete characterisation of organic sulphur species in coal.

The major error observed with the technique was the less than 100% recovery of pyrite as sulphur dioxide due to the partial conversion to H_2S. The other reason could be due to some conversion between functional groups. It was observed that a sample with high pyritic sulphur content the organic sulphur recovery was above 100%, whereas for a sample with lower pyritic sulphur content this was not observed.

The characterisation of various organic sulphur functional groups present in coal by the temperature programmed reduction method and later by the temperature programmed identification method confirmed that these methods can identify the organic sulphur groups in coal and that the results on the basis of total sulphur are comparable with standard analytical techniques. The analysis of the untreated and treated coal samples showed that the structural changes in the organic matrix due to a reaction can be determined.

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