

DETERMINATION OF SULFUR GASES FROM VELENJE COAL STOCKPILE**Janez Kozinc,^a Mireille Treeby,^a and Lucija Zupančič–Kralj^b**^a *ERICo Velenje, Institute for Ecological Research, Koroška 58, 3320-SI Velenje, Slovenia*^b *Faculty of Chemistry & Chemical Technology, University of Ljubljana, Aškerčeva 5, 1000-SI Ljubljana, Slovenia**Received 14-03-2004***Abstract**

Dimethyl sulfide (DMS), carbonyl sulfide (COS) and carbon disulfide (CS₂) were detected at the Velenje coal stockpile. The gases were collected in a sampling tent placed on the stockpile. Several sampling and measuring techniques were tested for their determination. For direct analysis and solid phase micro extraction (SPME) the gases were pumped from the tent into Tedlar bags, while for cryogenic trapping the gas was pumped through a cryo-trap from the tent. The analyses were performed by gas chromatographs, equipped with a flame photometric detector (FPD) and a mass selective detector (MSD).

It was found that direct gas analysis by GC-MSD is the method of choice for determination of the gases in the ppbv concentration level. DMS was rarely quantified, while concentrations of COS and CS₂ were temperature dependant. It was confirmed that oxygen was necessary for the formation of COS and CS₂. The source of COS and CS₂ is probably oxidation of pyrite in coal, which was determined by X-ray spectroscopy.

Key words: sulfur gases, oxidation of pyrite, coal stockpile, SPME

Introduction

Lignite, produced in the Velenje Coal Mine, Slovenia, is used as a fuel in the Šoštanj Thermal Power Plant. Due to its high coal consumption (755 MW power plant), it is necessary to keep a coal reserve in case of insufficient coal production. However, coal stockpiles involve problems such as environmental pollution and loss of coal calorific value. The volatile sulfur compounds (VSC) especially DMS, COS and CS₂ are also malodorous for living beings even at low concentration levels.

It has long been known that coal beds are reservoirs of gases, mainly carbon dioxide and methane. The desorption process begins when coal is mined and due to the presence of oxygen mined coal is also subject to oxidation. On the Velenje stockpile the minor product of these processes are also dimethyl sulfide (DMS), carbonyl sulfide (COS) and carbon disulfide (CS₂). It was found that the source of DMS from the lignite is desorption, while the presence of COS and CS₂ is probably the product of oxidation process.¹ Many authors investigated the presence of VSC in the neighborhood of

sulfide-bearing ore deposits.²⁻⁷ The experiments showed, that these gases, particularly COS, are related to the oxidation of pyrite, sphalerite and galena.⁵⁻⁷

The Verein der Deutschen Ingenieuren describes a direct method for gas sampling from a surface emission source.⁸ An airtight “tent” should be placed on the surface of the stockpile and after a certain time, a gas sample is taken. The gases from the tent can be pumped into a glass sampling cylinder, a rubber bladder or Teflon bags.

Gas chromatography is the method of choice for determination of VSC in air samples. The flame photometric detector (FPD) or mass selective detector (MSD) are appropriate detectors for determination of sulfur compounds, while the enrichment step of VSC can be done by cryogenic trapping, adsorption on solid surfaces (solid phase micro extraction), or chemisorption onto gold foil.⁹

The aim of our work was to develop and test methods for determination of sulfur gases (COS, CS₂ and DMS) collected from the coal surface and to assess their emission from the coal stockpile in Velenje.

Experimental

Sampling

The gas-tight polycarbonate sampling tent was placed on the stockpile and the emitted gases were collected in the tent. Its dimensions were 1 m in length, 1 m in width and 0.5 m in height. The total amount of stored lignite on the coal stockpile ranges between 50,000 and 800,000 tons and its surface varies between 60,000 and 120,000 m². Other characteristics of stored lignite on the stockpile are: calorific value 9,500-11,000 kJ/kg, moisture 37-43%, content of sulfur 1.5-1.9%. For direct analyses (without the preconcentration step) gas samples were taken from the sampling tent into 2 L Tedlar sampling bags. Moisture from the gas sampled was removed in the cold trap (0 – 4 °C). The gas for analyses was injected into the gas chromatograph (GC) directly from the bag via a sampling loop or using a gas-tight syringe.

Preconcentration by cryogenic trapping

The gas collected in the tent was pumped through a wet NaOH trap to remove carbon dioxide, through a cold trap (0-4 °C) to remove moisture and through the cryo-trap placed in liquid nitrogen. The components COS, CS₂ and DMS freeze at

temperatures -138.8 °C, -111.5 °C and -98.3 °C respectively. The flow through the trap was 0.67 L/min. After sampling the trap was heated and flushed with synthetic air and the released gases were collected in a 10 L Tedlar sampling bag.

Preconcentration with SPME fiber

The gas collected in the sampling tent was pumped through the cold trap (0-4 °C) where the moisture was removed and placed into 2 L Tedlar sampling bags. COS, CS₂ and DMS were preconcentrated on the 75 µm Carboxen-PDMS SPME fiber, which was introduced to the sampling bag. The extraction time was 15 min at ambient temperature.

GC analyses

The gas samples were analyzed using an HP 6890 gas chromatograph, equipped with an HP 5973 MS detector and a PE AutoSystemXL with an FPD detector. The GC operating conditions for both systems are listed in Table 1.

For qualification and quantification Messer's secondary gas standards for each gas component were used. Gas standards were diluted by an ECHO gas mixing chamber. In the sampling period, one sample was taken each day from the sampling tent situated on the stockpile. After sampling the tent was ventilated. For routine analysis direct GC-MSD was used. For comparison of different sampling methods, experiments with the two different sampling methods (cryogenic trapping and direct analysis) were performed.

Table 1. Operating conditions for HP 6890 and PE AutoSystemXL.

	HP 6980 ^a	PE AutoSystemXL ^b
Column	VOCOL 60m, 0.25mm id, 1.5µm film thickness	SUPEL-Q PLOT 30m, 0.53mm id
Carrier flow (He)	4 mL/min	0.5 mL/min
Inlet	splitless, 80°C ^c	sampling loop
Injection vol.	500 µL	100 µL
Oven temperature	50 °C, 1 min	35 °C, 10,5 min
Heating rate	18 °C/min to 170 °C	1: 5 °C/min to 57 °C 2: 120 °C/min to 180 °C, 5 min final time

^a Detector: MSD SIM mode (*m/z*): COS: 60, 62; CS₂: 76, 78; DMS: 62, 47, ^b FPD: Air flow: 100 mL/min; Hydrogen flow: 75 mL/min; Temperature: 300 °C, ^c When the gases were preconcentrated by SPME the inlet was heated to 250 °C, desorption time was 5 minutes.

Results and Discussion

In Table 2 measurement characteristics of chromatographs are shown. For the methods with the MSD detector (SPME and direct analyses), a calibration curve was recorded every measuring day, while with the FPD detector calibration curves were stable for at least one year. For the limits of detection (LOD) and quantification (LOQ) spiked samples which gave detectable responses were measured. For estimation of LOD and LOQ 3s (s =standard deviation) and 10s of measurements was added to the known concentration of spiked samples.

Table 2. Some characteristics for different measuring methods.

Parameter		GC-FPD	GC-MS
LOD	COS	0.5 ppm	5.2 ppb
	CS ₂	0.1 ppm	8.8 ppb
	DMS	0.3 ppm	3.0 ppb
LOQ	COS	1.1 ppm	6.4 ppb
	CS ₂	0.2 ppm	12.5 ppb
	DMS	0.6 ppm	4.2 ppb
Linearity	COS	R ² >0.99	R ² > 0.99
	CS ₂	R ² >0.99	R ² > 0.99
	DMS	R ² >0.99	R ² > 0.99
Working range	COS	10 – 50 ppm	26 – 1000 ppb
	CS ₂	10 – 50 ppm	24 – 1000 ppb
	DMS	1 – 100 ppm	8 – 350 ppb
Peak resolution	COS	} R=1.42	
	CS ₂		
	DMS		

Peak resolution (R) is more than 2 where not stated differently.

Initially a GC with an FPD detector was used for determination of VSC. As the concentrations of gas components in the samples from the coal pile were below the first point of the calibration curve, a preconcentration step by cryogenic trapping was performed. Moisture and small amounts of CO₂ caused the flow through the cryo-trap to stop even though the NaOH trap for CO₂ and cold trap for moisture removal were used. The NaOH trap lowered the concentration of CS₂ and DMS by 13 and 10%. Another disadvantage was low resolution between DMS and CS₂ with the SUPEL Q column.

The experiments showed that the recoveries of the preconcentrating procedure by cryo-trap are 65% for DMS, 59% for CS₂ and 69% for COS. Assessed RSD of the

recovery study are 5.1, 3.2 and 6.7% for COS, CS₂ and DMS (4 replicates). Other disadvantages of such sampling are time consumption, complicated sampling equipment and transportation of frozen samples to the laboratory. The VSC were enriched 12 to 15 times by this procedure. By the use of a smaller sampling bag the gases can be better enriched after heating and flushing of pre-concentrated gases from the cryo-trap.

To avoid the disadvantages described above, a better detection system or a simpler pre-concentration technique can be used. A gas chromatograph, equipped with a VOCOL column offered good separation between CS₂ and DMS ($R > 2$) and connected to the mass selective detector it was sensitive enough to detect COS and CS₂ directly from the gas sample. DMS was quantified only a few times by direct GC-MSD, because it was mainly desorbed from the coal before the experiments were performed.

In Table 3 the results of parallel determination of VSC after each method of sampling are presented. In the case of cryo-trapping the recoveries (65, 59, and 69%) were taken into account for calculation of final gas concentrations. The flow through cryo-trap was 40 L/h and the total amount of gas passed through the trap was 120 L on 11th August and 140 L on 10th and 12th August 2003.

Table 3. COS, CS₂ and DMS concentrations (ppb), in the gas samples determined by direct analysis and via cryogenic trapping.

Date	Direct determination			Cryo-trap		
	COS	CS ₂	DMS	COS	CS ₂	DMS
10.8.2003	240	165	10	215	147	8
11.8.2003	356	263	<8	365	266	<8
12.8.2003	244	151	<8	227	135	<8

The differences between direct determination and via cryogenic trapping are not significant. As the concentration of DMS was determined only four times during the sampling period by direct injection, SPME sampling was tested to achieve lower LOD for DMS. CAR-PDMS is a solid coating onto which the analytes are adsorbed and as adsorption sites are limited, competitive adsorption and displacement can occur.¹⁰ To determine the extraction efficiency of the gases by SPME, different mixtures of the gases were analyzed. The average peak areas of COS, CS₂ and DMS are presented in Table 4.

It is seen from Table 4 that displacement of DMS occurred when CS₂ and COS were present. The average peak area of DMS is approximately 16% lower in case of the gas mixture (COS, CS₂ and DMS in air). To avoid this limitation the gas components in calibration standards should be prepared in the same concentration ratio as they are in a sample. Due to variability of VSC concentrations in samples, preparation of calibration standards can be time-consuming. The repeatability (expressed as RSD) of 4 replicates is less than 3%. Achieved LOD for DMS by SPME was approximately 40 ppt.

Table 4. Average peak areas of COS, CS₂ and DMS in different gas mixtures.

Gas	COS		DMS		CS ₂	
	Concentration	Area (10 ³)	Concentration	Area (10 ³)	Concentration	Area (10 ³)
1. mixture	200 ppb	10	87 ppb	23	254 ppb	140
2. mixture	0 ppb (ambient air)	0	87 ppb	27	0 ppb (ambient air)	0

The results in Figure 1 show that concentrations lines of COS and CS₂ have the same trend as temperature, although there is not a direct correlation between them. While COS and CS₂ were quantified almost every day DMS was quantified only four times which was expected as our stockpile was made approximately a year previous to the date of our sampling period. As has been shown the source of DMS from coal is the desorption process and the concentration of DMS fell to less than 1 ppm in a few days.¹

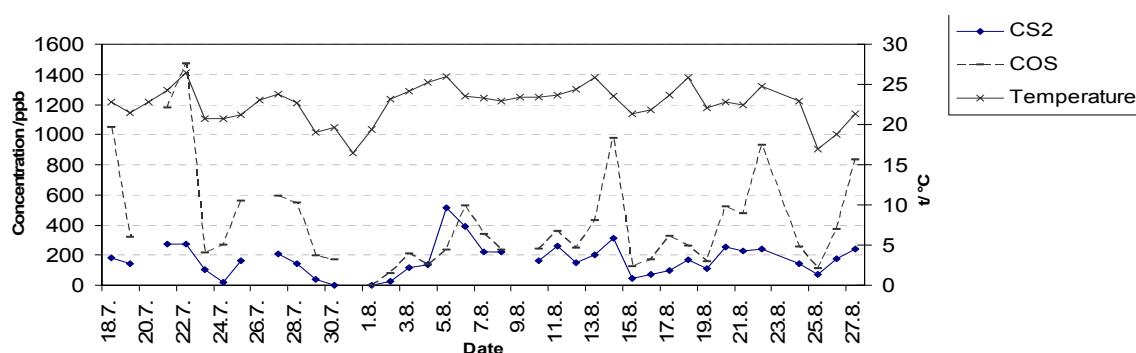


Figure 1. Concentrations of COS and CS₂ versus temperature in gas samples from coal stockpile.

Regarding the previous investigations the source of COS and CS₂ in the lignite is probably oxidation of pyrite. Its presence was confirmed by X-ray spectroscopy. The content of sulfide sulfur ranged between 0,3 to 0,4 w% in the coal from the pile.

To confirm the formation of VSC two coal samples were incubated in different atmospheres and temperatures. Two coal samples were dried at 30 °C to constant mass

(DIN 51718), ground to powder (<0.2 mm particle size) and than put into 20 mL vials which were crimped. Half of them were filled with nitrogen (99,999%) while the other half was filled with synthetic air. A quarter was than incubated at 70 °C, another quarter was kept at 25 °C in the dark. Four replicates for each quarter were prepared. After four days of incubation the atmospheres above the coal samples were analyzed. The results for both samples are presented in Table 5.

Table 5. Concentrations (ppb) of COS, CS₂ and DMS in glass vials after 4 days of incubation.

Atmosphere in the vial	Component	Incubation at 25 °C		Incubation at 70 °C	
		Sample 1	Sample 2	Sample 1	Sample 2
Nitrogen	CS ₂	<24	<24	39	44
	COS	74	69	201	221
	DMS	<8	<8	45	26
Synthetic air	CS ₂	<24	<24	293	342
	COS	560	502	1444	1682
	DMS	<8	<8	82	37

In both samples the concentrations of measured gases were lower in the vials which were flushed with nitrogen. As shown in Table 5, synthetic air plays an important role in the formation of COS and CS₂, particularly when the incubation temperature is high. In the vials containing nitrogen the concentrations of CS₂ and DMS were under the quantification limit, only COS was quantified in this case. Its concentration was approximately 7 times higher in the vials filled with synthetic air, confirming the results from previous studies that the source of COS is oxidation. The presence of COS in the vials filled with nitrogen was probably the consequence of the coal samples' exposition to air before being placed into the vials and due to trace amounts of oxygen in the vials.

When the incubation temperature was higher (70 °C) all the gases were determined. The increase in CS₂ concentration in the vials with synthetic air in comparison to the vials filled with nitrogen showed that more CS₂ was formed in the presence of oxygen. The concentrations of COS and CS₂ are several times higher (7 to 8) in the case of the vials filled with synthetic air to those filled with nitrogen. The RSD of the whole procedure (sampling of coal, preparation of the vials, measurements) is less than 20%.

A similar effect to the one in the vials was observed on the stockpile, where at higher air temperatures higher concentrations of COS and CS₂ were determined in the gas samples taken. The estimated daily emissions of COS and CS₂ for the whole stockpile in the sampling period were 20 g CS₂ and 70 g COS.

Conclusion

Emissions of COS, CS₂ and DMS were studied from the coal stockpile in Velenje. Several techniques were used for preconcentration and analyses. At first the gas was pre-concentrated from the tent in a cryo-trap via NaOH for CO₂ removal, and subsequent analyses of gases released from the trap were performed by GC-FPD. As the method was complicated the method for determination of VSC on GC-MSD was developed. With this method the preconcentration step was not needed for determination of a few ppb COS, CS₂ and DMS.

The results show that concentrations of COS and CS₂ are influenced by temperature and that oxygen is required for their formation. The presence of oxygen does not have an influence on the concentration of DMS in the same way as temperature does.

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Povzetek

Na odlagališču premoga v Velenju so bili zaznani plini dimetilsulfid (DMS), karbonilsulfid (COS) in ogljikov disulfid (CS₂). Plini so bili ulovljeni v vzorčevalni šotor, postavljen na vrh odlagališča. Zaradi nizkih koncentracij plinov so bili poleg direktnega določevanja opravljene različni poskusi koncentriranja omenjenih plinov – vzorčenje v hladno past in adsorpcija na SPME. Analize plinov so bile opravljene s plinskima kromatografoma s plamensko fotometričnim detektorjem (FPD) in masno selektivnim detektorjem (MSD). Kot najustreznejši način določevanja plinov v območju ppb se je izkazala neposredna določitev z GC-MSD, brez koncentriranja. Dimetilsulfid je bil le redkokdaj določen, koncentracije COS in CS₂ pa so temperaturno odvisne. Z laboratorijskimi poskusi je bilo potrjeno, da je prisotnost kisika nujno potrebna za nastanek COS in CS₂. Vir COS in CS₂ je torej verjetno oksidacija pirita v premogu, ki je bil dokazan z rentgensko spektroskopijo.