Thermochimica Acta, 134 (1988) 435–440
Elsevier Science Publishers B.V., Amsterdam

UTILIZATION OF DIFFERENTIAL SCANNING CALORIMETRY TECHNIQUE FOR DETERMINATION OF HIGH SULFUR CONTENT

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ABSTRACT

The determination of a high sulfur content in solid samples by Differential Scanning Calorimetry (DSC) was investigated and shown to be feasible.

Experimental data have indicated that the DSC peak area of sulfur melting is proportional to the sulfur weight present in the sample. The (peak area/sample weight) ratio (A/W) is a function of sulfur content; high sulfur content results in high A/W.

Elemental sulfur content in solid samples is quickly determined by DSC and the accuracy of this method is comparable with that of carbon disulfide (CS_2) extraction.

INTRODUCTION

Quantitative determinations of high elemental sulfur content in solid samples are usually very time consuming techniques which often need more than one step. This can be observed in techniques such as solvent extraction, gravimetry, calorimetry and direct ignition[1](ash).

X-ray fluorescence gives semi-quantitative results, while quantitative determination using LECO apparatus is limited to low sulfur content samples.

Elemental sulfur content can be rapidly determined in a single operation using the DSC technique. Here the melting peak area of elemental sulfur of a sample is proportional to the sulfur content and is compared with the melting peak area of a standard sulfur sample.

In this work industrial sulfur waste samples were used from sulfuric acid plants which use elemental sulfur as starting material.

Thermal Analysis Proc. 9th ICTA Congress, Jerusalem, Israel, 21–25 Aug. 1988
0040-6031/88/$03.50

EXPERIMENTAL

A DuPont 9900 thermal analyser with a DSC cell attachment was used, in the following operation conditions:

Nitrogen flow = 60 ml/min

Starting temperature Ti = 80°C

Heating rate = 2°C/min

Final temperature Tf = 130°C

Sample container = aluminium sealed pan

The sulfur waste samples used in this experiment are formed by a heterogeneous physical mixture of elemental sulfur (60-90%), diatomaceous earth and some gypsum.

In order to have representative samples, the waste materials were sized at 200/325 mesh and quartered.

Also prepared were synthetic mixtures using known elemental sulfur weights, previously melted in a thermostatic bath at 140°C with stirring. The mixture was cooled, crushed, sized at 200/325 mesh and quartered.

The standard sample used for DSC daily calibration was a sublimated sulfur from Merck (99,99%).

All the waste and standard samples were dried at 80°C for 4 hours under vacuum.

DSC experimental data were compared with those obtained by the CS_2 extraction method data analysis[2]. Sulfur (3 g of each sample) was extracted for 1 hour in 50 ml of boiling (CS_2) which was then distilled and the extracted sulfur was vacuum-dried.

RESULTS AND DISCUSSION

Table 1 shows the DSC data for analysis of standard sulfur.

Figure 1 shows the representative curve of sulfur weight versus the melting peak area of the DSC, where a linear correlation between sulfur weight and the area of the melting peak was observed.

Figures 2, 3 and 4 present typical DSC thermograms of sulfur samples.

TABLE 1 - DSC DATA FOR STANDARD SULFUR

WEIGHT (mg)	AREA	AREA/WEIGHT
0,6250	7,25	11,60
1,2880	14,91	11,58
2,1930	25,98	11,85
2,9300	34,95	11,93
4,1370	48,44	11,71
5,1550	59,07	11,46

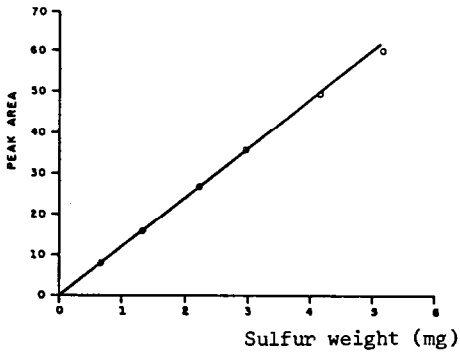

Fig 1:SULFUR WEIGHT VERSUS MELTING PEAK AREA

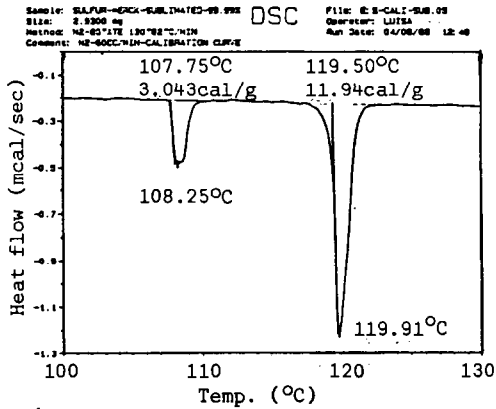

Fig 2:TYPICAL DSC CURVE OF STANDARD

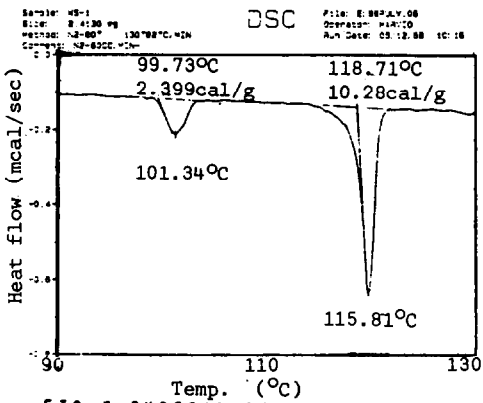

FIG 3:TYPICAL DSC CURVE OF WASTE SAMPLE

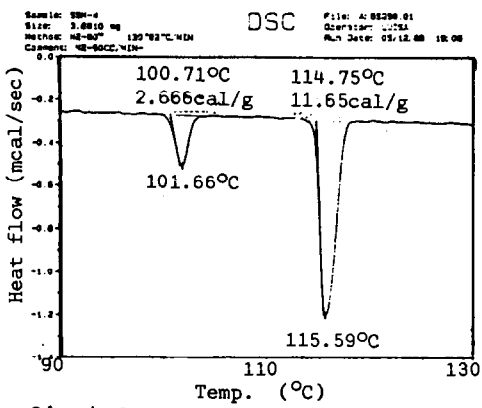

Fig 4:TYPICAL DSC CURVE OF SYNTHETIC MIXTURES

Table 2 presents experimental data for sulfur wastes (SW) and sulfur synthetic mixture samples (SSM) related to DSC and CS_2 extraction analysis. Sulfur content by DSC was calculated by:

$$\% S = \frac{(area/g)sample}{(area/g)standard} \times 100$$

TABLE 2 - DSC DATA AND CS_2 EXTRACTION FOR SW AND SSM SAMPLES

SAMPLE Nº	SAMPLE WEIGHT (mg)	DSC AREA/MASS	% S FROM DSC	% S FROM CS_2 1 x C
WS-1	2,2470	10,24	86,6	89,3
	2,4130	10,23	86,5	
	2,2900	10,13	86,4	
	2,2470	10,24	87,3	
	2,4130	10,23	87,2	
WS-2	2,2770	9,61	82,0	83,3
	2,2480	9,61	82,0	
	2,3300	9,57	81,6	
WS-3	2,2720	10,91	93,0	97,3
	2,4010	10,94	93,2	
WS-4				83,0
	2,4890	9,42	80,3	
	2,2030	9,92	84,6	
WS-5	2,4640	11,69	98,9	99,9
	2,3740	11,78	99,7	
WS-6	2,3880	7,96	67,3	68,1
	2,3570	7,74	64,5	
SSM1	2,2360	5,44	46,4	54,6
	2,5250	5,65	48,2	
	4,8960	5,73	48,8	

SSM2	2,4250	8,35	71,2	70,0
	2,1980	8,07	68,8	
	2,4580	8,07	68,9	
SSM3	2,5710	10,01	84,7	82,3
	2,5060	10,08	85,3	
SSM4	3,8810		99,1	98,1
	2,4200	11,65	98,6	

Experimental data shows that:

- sulfur DSC thermograms present two peaks: The first represents the rhombic to monoclinic transition, and the second, the melting of sulfur (3).

- for different weights of standard sulfur, constant peak area per weight values were observed for both the transition (2,97) and melting (11,73) points.

- the relationship between sulfur weight and the area of the melting peak in the DSC thermogram is linear.

- it is possible to determine quantitatively the sulfur content of a sample dividing the melting peak area per unit weight of the sample by the melting peak area per unit weight of the standard.

- it is not possible to determine quantitatively the sulfur content of a sample by using the transition peak data because the relation (peak area/sulfur weight) is not linear, as observed.

- besides having a good repeatability, the data obtained from the DSC analysis agree with those obtained by CS_2 extraction.

CONCLUSIONS

Preliminary experimental data show that the DSC technique is a powerful tool for quickly determining high elemental sulfur contents in solid samples.

At present, statistical data to determine the precision and the accuracy of this method are under investigation in our laboratory and we expect to publish these results shortly.

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