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DETERMINATION OF THE TOTAL SULPHUR CONTENT IN GAS OILS WITH A FLAME PHOTOMETRIC DETECTOR

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SUMMARY

A method is described for the quantitative determination of the total sulphur content of gas oils, using a gas chromatograph with an empty glass column and a dual-flame flame photometric detector. The method can also be used for the analysis of the volatile sulphur content in aqueous solutions.

INTRODUCTION

During a study of catalytic hydrodesulphurization of gas oils[1] a method was needed not only for the determination of the distribution of sulphur compounds, but also, more importantly, for the determination of total sulphur content. Methods have been published for the determination of the distribution of sulphur compounds in gas oils using gas chromatography (GC) with a coulometric detector[2,3]. The flame photometric detector (FPD) has proved its usefulness for the analysis of sulphur compounds. The response of the FPD for nanogram amounts of sulphur is comparable with that of the microcoulometric detector[4].

The dual-flame concept was introduced to improve the FPD performance[5,6]. The work of Rupprecht and Phillips[6] is of particular interest, since the system was used not only as a GC detector but also for the continuous monitoring of the odorant sulphur content in hydrocarbon gases and the determination of sulphur content in volatile liquids. Difficult operation and somewhat poor reproducibility apparently prohibited a more widespread use. These problems seem to be greatly reduced in a more recent design[7].

In this paper a simple method is described for the quantitative determination of the total sulphur content in oil fractions, using a gas chromatograph with an empty glass column and a dual-flame FPD. The method was extended to the determination of the total (volatile) sulphur content of aqueous solutions. This was applied to a scrubber for gasifier effluents.

EXPERIMENTAL

Because of the non-linear response of the FPD, the simplest approach was to

elute all sulphur compounds in one peak, preferably with reproducible peak width. The samples were rapidly evaporated in an injector at relatively high temperature. The vapour was then led through an empty glass column of length 3 m before reaching the detector, to prevent a sudden pressure rise in the detector, extinction of the flames, and errors caused by too low response of the detector system.

The usual injection method yielded non-reproducible results. However, when only the needle volume of a standard Hamilton 10-μl syringe (701N) was injected during exactly 5 sec, a reproducible injection volume of *ca.* 0.5 μl was obtained.

The non-linearity of the FPD made careful calibration necessary. For gas oils calibration was performed in two ways:

(1) A standard reference oil containing sulphur was diluted (w/w) with the same type of oil, but absolutely free from sulphur;

(2) A series of reference oil samples was measured independently.

The sulphur amounts of reference samples were checked by X-ray fluorescence, using the method of standard additions.

For aqueous solutions calibration was performed by injection of solutions of known concentration of thioacetamide in water. The detector responses were compared for a series of six compounds dissolved in water.

Conditions

A gas chromatograph Varian 3700 with a dual-flame FPD was used under the following conditions: column, empty glass column, 3 m × 0.25 in. O.D.; injector temperature, 320°C; column oven temperature, 300°C; FPD block temperature, 240°C; injection, 0.5 μl; carrier gas, helium, at a flow-rate of 3 ml/min for oil, 20 ml/min for aqueous solutions; characteristic retention time, 250 sec for oil, 40 sec for aqueous solutions; integrator, Infotronics 304.

RESULTS

The detector responses for two series of oil samples are presented in Fig. 1. The two series coincided on the same calibration curve. In this case the detector electronics were operated in the "root" mode. The curve shows an exponential relationship; the concentration dependence exponent is 0.82, corresponding to $n = 1.64$ in the normal mode. The relative accuracy was 2 % at the 1 % level and 10 % at the 100 ppm level of sulphur percentage.

The results of the analysis of a characteristic series of oil samples (before and after desulphurization) are listed in Table I. For these samples the sulphur contents were checked by X-ray fluorescence. Reference samples were injected between the regular samples.

Table II summarizes the detector responses for a series of aqueous solutions. In this case the detector electronics were operated in the "direct" mode. Again an exponential relationship was found with $n = 1.76 \pm 0.05$.

In a separate experiment a mixture was prepared of 15 ml of the aqueous thioacetamide solution and 1 ml of the aqueous solutions of the other compounds listed in Table II, all solutions containing 800 mg/l. Analysis of this mixture as described above, using the thioacetamide calibration curve, yielded a sulphur peak area of $190 \cdot 10^5$ counts/sec, corresponding to a sulphur concentration of *ca.* 815 mg/l.
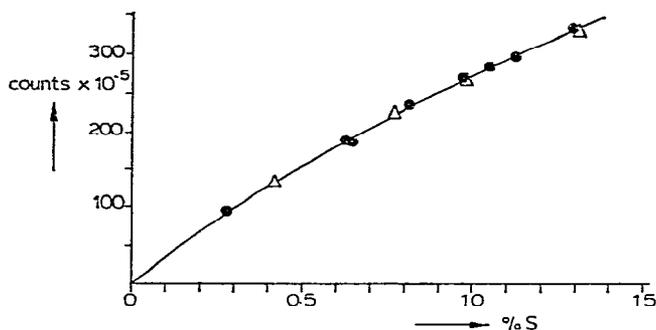
Fig. 1. Calibration curve for the determination of total sulphur content in oils ($\triangle$ = diluted sample, $\bullet$ = independent sample).

TABLE I

DETERMINATION OF TOTAL SULPHUR CONTENT IN GAS OILS

Samples 1–5 are distillation fractions of a virgin oil.

Sample	Sulphur (%, w/w)	
	GC	X-ray
1, Untreated	1.03	1.02
2, Untreated	1.35	1.31
3, Untreated	1.44	1.40
4, Untreated	1.80	1.75
5, Untreated	2.09	2.11
1, Desulphurized	0.015	0.014
2, Desulphurized	0.013	0.013
3, Desulphurized	0.021	0.024
4, Desulphurized	0.011	0.021
5, Desulphurized	0.084	0.082
Virgin oil, original	1.54	1.55
Virgin oil, desulfurized	0.046	0.044

TABLE II

DETECTOR RESPONSES (PEAK AREA) FOR SIX COMPOUNDS IN WATER (VALUES IN INTEGRATOR COUNTS $\times$ 10^{-5})

Compound	Concentration of sulphur (mg/l)			n
	200	400	800	
Thioacetamide	16.7	53.1	183	1.73
Dimethyl sulphoxide	15.0	52.4	186	1.82
Sulpholane	16.0	55.8	181	1.75
Dimethylsulpholane	16.9	55.1	177	1.69
3-Methylsulpholene	16.3	63.4	192	1.78
3,3-Thiodipropionitrile	15.6	49.2	192	1.81
Mean	16.1	54.8	185.2	1.76
S.D.	0.7	4.8	6.0	0.05

DISCUSSION

Several authors[1,8-10] have found different relative response orders of sulphur compounds when using a single-flame FPD. However, Burnett et al.[11] showed that the actual FPD response order of those compounds depends on the concentrations or ranges of concentrations being examined. For a series of eleven sulphur compounds they found exponential proportionality constants n between 1.48 and 2.00. Maruyama and Kakemoto[12] found that the response to sulphur compounds (containing C_1–C_{12}) was dependent only on the number of sulphur atoms in a molecule and not on its structure.

The dual-flame FPD seems to have overcome many of these problems[7]. Patterson[13] found a pure square-law dependence for thirteen compounds, including methyl mercaptan, hydrogen sulphide, sulphur dioxide and parathion, and an equal response per nanogram of sulphur for methyl parathion and hexanethiol. Gangwal and Wagoner[14] slightly amended these results. They plotted the value area·height$^{-\frac{1}{2}}$ versus sulphur content, and found slopes of 0.92 for H_2S, COS and SO_2, 0.93 for methyl mercaptan and thiophene, and 0.85 for CS_2, corresponding to $n = 1.84$, 1.86 and 1.70, respectively. Equal responses were found for ca. 5 ng of each compound.

Despite the fact that in our work all sulphur compounds are coeluted on top of the bulk of the organic material (oil) or water, the constant n is of the order of 1.64 for oil and 1.7–1.8 for aqueous solutions; the absolute responses are highly comparable in the latter case. This proves that even under our rather extreme conditions the detector is still working properly. Deviations from the square-law dependence may be explained by deviation of the Gaussian shape, tailing and change in peak width with sulphur mass[14], or change in flame temperature or composition and concentration of free-radical species in the flame[11].

CONCLUSION

It is possible to determine total (volatile) sulphur contents in oil and water, using GC with an empty glass column and dual-flame FPD. The method is simple and can be performed by the same person carrying out other GC analyses, without any further special experience or apparatus, thus avoiding laborious micro-elemental analysis.

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