Critical Appraisal of the Flame Photometric Detector in Petroleum Analysis

D. A. Ferguson / L. A. Luke
The British Petroleum Company Limited BP Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex, Great Britain

Key Words
Flame photometric detector
Petroleum analysis
Sulphur selective detector
Organo-sulphur compounds

Summary
This paper summarises experience gained at the British Petroleum Limited Research Centre, Sunbury-on-Thames, with sulphur selective gas chromatography (GC) detectors. A single flame photometric detector (SFPD) has been in use for three years for research and routine applications. Three areas of interest are described demonstrating in turn different characteristics of the detector. Firstly, a determination of trace levels of individual organo-sulphur compounds in the 15-65°C cut of crude oils illustrates the complexity of using an SFPD in a rigorously quantitative manner. Secondly, the use of an SFPD as a qualitative tool for the comparison of the sulphur distribution of crude oils up to the temperature limit of GC is cited. Finally, a third section describes the properties of a dual flame photometric detector (DFPD) which are compared and contrasted with those of the SFPD.

Introduction
The single flame photometric detector (SFPD) used until recently at the BP Research Centre, Sunbury, was manufactured by Pye Unicam Limited, Cambridge, England. It is based on an original design by Brody and Chaney [1] and its properties are described by Moss [2]. A simplified diagram appears in Fig. 1.

The column effluent containing organo-sulphur compounds and hydrocarbons enters the detector assembly and passes up an annular space where it is mixed with hydrogen (30 cm³/min⁻¹). Meanwhile, air (30 cm³/min⁻¹) enters the detector via the axial tube. At the top of the concentric assembly the gases are ignited to produce a hydrogen-rich diffusion flame. Within this flame the reducing zone is responsible for the conversion of sulphur atoms in organo-sulphur compounds to a transient excited diatomic species, S₂⁺. The electronic transitions of this species produce a number of emission bands. The most intense is at 394 nm. The radiation passes through a Pyrex chimney and impinges upon a narrow band-pass optical filter which permits only a narrow band of light around 394 nm to fall upon a photomultiplier tube. The consequent cascade of electrons provides the signal that is finally amplified and recorded.

In spite of the simplicity of the basic concept the SFPD has three unfortunate characteristics which constitute major problems for the petroleum analyst.

1 Inequality of Response
The response of a mass detector should be characterised by the following equation:

\[ y = AM^r \]

where \( y \) = detector response, \( A \) = constant, \( M \) = quantity detected, \( r \) = response index.

Ideally, for a truly linear detector, \( r = 1 \), However, in the case of all flame photometric detectors, because the emitting species is formed from two sulphur atoms, theory demands that the value of \( r \) should be two, i.e. quadratic response [2, 4, 5]. This simply means that doubling the quantity detected should result in a four-fold increase in response.

Although the quadratic response may be inconvenient it could be accommodated if in practice it were true. In fact, our own experience and the experience of many other workers, e.g. [2, 4, 5] indicates that the value of \( r \) is not constant for all sulphur compounds. Values of \( r \) lying between 1.5 and 2.1 are commonly encountered. The implication of this is that if the SFPD is to be used in a rigorously quantitative manner all compounds of interest must be calibrated individually. A systematic method of predicting the response index with any acceptable degree of accuracy is not currently available.
Plainly, in petroleum analysis where the number of organo-sulphur compounds is very great and largely unidentified, calibration on this scale is impossible except, perhaps, for very narrow boiling cuts.

2 Quenching of Sulphur Response

This potentially disastrous situation arises when a large quantity of hydrocarbon co-elutes with an organo-sulphur compound. Even a moderate excess of hydrocarbon can prevent the propagation of the crucial S* to such an extent that the sulphur response is entirely eliminated.

Since, in petroleum, there is inevitably a superabundance of hydrocarbons throughout the entire boiling range accessible to gas chromatography (GC), this problem is unavoidable. The only method of overcoming the quenching effect is to select a GC column which will separate the organo-sulphur components from all the hydrocarbons. However, this solution is impracticable except for very narrow boiling cuts.

3 Lack of Selectivity

Although the amount of radiation produced by hydrocarbons near the critical wave-length is small compared with sulphur species, the inevitable large excess of the former frequently means that it is responsible for a significant proportion of the detector response. Because the SFPD sulphur response is quasi-quadratic and its residual hydrocarbon response is linear, the selectivity ratio decreases as the level of sulphur decreases with respect to hydrocarbon. Therefore, the lack of selectivity becomes most significant for trace sulphur levels, which is precisely the application that requires the maximum selectivity.

Applications

1 Analysis of Individual Sulphur Compounds in the 15 °C to 65 °C Cut of Crude Oils

This work is described briefly to show the complexity of overcoming the inequality of response, quenching and lack of selectivity problems of the SFPD. This ought to be one of the simplest sulphur analyses in petroleum chemistry because this narrow boiling range contains a mere half-dozen organo-sulphur compounds together with no more than 20 potentially co-eluting hydrocarbons. Apart from the problems of chromatographing trace quantities (typically 1–100 ppm) of highly polar and unstable alkyl thiols, the analysis reduced to a calibration exercise to overcome inequality of response and a separation exercise to overcome the quenching and selectivity problems.

A long term calibration of the detector by conventional gravimetric blending techniques was not sufficiently accurate due to the instability of the blends. Technically the problem was solved most satisfactorily by the permeation tube method [6]. However, the development of the permeation tube calibration technique for low levels of alkyl thiols and alkyl sulphides required an immense effort in comparison to a conventional gravimetric approach. Indeed, the development of the permeation tube method constituted a major project alone.

Fig. 2 illustrates the calibration curve obtained for the four alkyl thiols (methane thiol, ethane thiol, 2-methyl-propane-2-thiol and propane-1-thiol) and two alkyl sulphides (dimethyl sulphide and methyl ethyl sulphide) present in the fraction by the permeation tube method. The values of the response index calculated from this plot lie between 1.8 and 2.1. There appeared to be no identifiable relationship between each compound and its r value. The linear range of the detector extended from ca. 1 ppm to ca. 300 ppm.

Similarly, the choice of a GC column was a protracted affair. The essential property of the column was that it should retain methane thiol (boiling point 6 °C), the lowest boiling organo-sulphur compound of interest in the fraction, longer than n-hexane (boiling point 69 °C) which was the highest boiling hydrocarbon likely to be present in significant quantities. In addition, the column had to separate the individual sulphur compounds from each other. Examination of several polar liquid phases failed to discover any with the correct combination of hydrocarbon/sulphur selectivity and sulphur compound separation. However, by calculating the relative retention data of sulphur compounds and n-alkanes on various polar phases it was predicted that a combination of 40% by weight tri-