

CHROMSYMP. 2674

# Simultaneous determination of sub-mg/l levels of sulphur and chlorine in liquid hydrocarbons by a coupled combustion–ion chromatography technique

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## ABSTRACT

A method for elemental analysis that employs a novel coupled combustion–ion chromatography (C–IC) apparatus is described in detail. The samples are combusted and the products collected in a dilute peroxide solution. This solution is loaded onto a concentrator column which is then introduced into the injection position of a suppressed conductivity anion chromatography system. The method is rapid, reliable, free from interferences and has the capacity for simultaneous determination of sulphur and chlorine in organic liquids at concentrations down to 0.03 mg/l. Provided that the capacity of the concentrator column is not exceeded, the recovery for organic standards of both chlorine and sulphur in a variety of organic solvents is greater than 93%, irrespective of the solvent and the sample volume and concentration. Repeatability is only slightly worse than that observed for conventional direct IC analysis of aqueous solutions. At concentrations of 0.4 mg/l Cl and 0.5 mg/l S, the % standard deviations ( $n = 10$ ) were found to be 2.9 and 3.5% respectively. The results obtained with the C–IC analyser for both standards and petroleum-based samples are in good agreement with those obtained by microcoulometry.

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## INTRODUCTION

Organo-sulphur and organo-chlorine are well documented poisons of catalysts [1–3]. Since catalysts are used in a wide variety of applications in the petroleum industry [4], close monitoring of these species in feeds and products from various petroleum and petrochemical processes is essential in order to meet modern process specifications and to avoid loss of catalyst activity. At BP, microcoulometry (oxidative) [5–8] had been used since the early 1970s for such monitoring and had become the established technique within the petroleum industry for both sulphur [9] and chlorine [10]. However, these methods had several inherent problems associated with them:

(i) As separate electrolytic cells are required for sulphur and chlorine analysis, simultaneous determination of sulphur and chlorine is not possible. Thus, analysis for both elements by microcoulometric techniques involves two calibration procedures and changing the cell configuration. Furthermore, the stabilisation time between the changing of cells had been found to be excessive (average 3–4 h), particularly when changing from sulphur to chlorine.

(ii) Day-to-day variation in cell performance, particularly the chlorine cell, required the full-time attention of an experienced analyst to balance the settings for amplifier gain and bias in order to obtain the optimum peak response to facilitate accurate quantification.

(iii) Both organic bromine and organic iodine species interfered with the chlorine analysis since they form entities which are titrated in the cell.

(iv) In the combustion of organo-sulphur species,

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sulphur trioxide as well as sulphur dioxide is produced because of the strongly oxidative nature of the conditions used. Since only sulphur dioxide is titrated in the cell, accurate quantification relies on samples and standards combusting to give the same dioxide:trioxide ratio. In practice, depending on the combustion temperature and oxygen concentration, this ratio may vary for different organo-sulphur species [8]. SO<sub>2</sub> conversion is normally above 90% but, within the terms of the IP methods [9,10] can be as low as 75% and still be acceptable.

These problems, coupled to sensitivity limitations, led to the requirement for an alternative method that could determine, simultaneously, trace levels of organo-sulphur and organo-chlorine compounds in organic media.

In 1988 a brief overview of ion chromatography (IC) in the oil industry [11] highlighted its potential for simultaneous multi-elemental analysis. To accommodate elemental analysis in organic materials a combustion stage prior to IC analysis may be applied [12]. Combustion of the sample followed by IC analysis had been used to determine the halogens, sulphur, phosphorus and selenium and had been applied successfully to coal and oil shale [13] using a Parr oxygen bomb, fuel oils [14] and other organic materials [15,16] employing Schöniger oxygen flask combustion, and to silicate rocks [17] with a furnace combustion set-up. However, all these analyses involved a distinctly separate combustion stage, followed by IC analysis of the combustion products after absorption into a suitable media. Meador [11] suggested that a combination of combustion and IC in one instrument would greatly enhance the technique, making it simple and rapid to operate, and rendering it more suitable to automation. Furthermore, with the introduction of a concentrator column [18] the method would permit analysis of chlorine and sulphur at sub ppm levels, and thus provide a more sensitive alternative to microcoulometry. This paper describes the development between 1987–1988 of such an analyser. It concludes a detailed description of the coupling of the tube furnace combustion stage to the ion chromatography module with a suitable "small volume" bubbler, and compares the results obtained with microcoulometric determinations.

Since this work, further combustion-ion chromatography (C-IC) studies have been reported, cov-

ering applications in the pharmaceuticals [19], paper [20], edible oil [21,22] and oil and petrochemicals [23–25] industries. However, these studies have continued to use a separate combustion stage, either by Schöniger oxygen flask [19,20,26,27], Parr oxygen bomb [21,22], PTFE Parr bomb [23] or tube furnace [24,25,28]. Due to the limitations on combustion mass, the volumes of absorber required, and the absence of a concentration stage, studies reported in the literature invariably have higher limits of detection (LODs) than that reported in this study. Only Assenmacher and Frigge [24] have described a combination of combustion followed by IC capable of measurement at sub-ppm levels, using large sample masses and absorber volumes of 50 ml. Thus, with respect to both sensitivity and the elegant combination of the combustion and IC stages, the work described here compares favourably with the C-IC studies published to date.

## EXPERIMENTAL

### *Instrumentation*

C-IC analyses were carried out on the C-IC analyser developed during this study. A schematic diagram and photograph of the C-IC analyser are shown in Figs. 1 and 2, respectively. Essentially the analyser consists of three modules as detailed below.

*Sample combustion module.* This consists of a twin-tube furnace (Carbolite CFM 12/2) set at 900°C. Gas flows (helium and oxygen) through the system are controlled by needle valves and measured by 0–250 ml/min Gas meters. The furnace houses two silica combustion tubes—one single-chamber tube (used for oxygen purification) and one two-chamber tube (used for sample combustion).

The oxygen used for sample combustion is passed through the first (single-chamber) combustion tube (length, 300 mm; diameter, 22 mm) where any trace organic impurities present are converted to the corresponding acidic combustion products, hydrogen chloride, sulphur dioxide and sulphur trioxide. The hot oxygen then passes through an absorber train comprising three 125-ml Dreschel bottles, the first two of which contain 50 ml of 50% sodium hydroxide to remove both the acidic combustion products of organic impurities and any trace inorganic impu-

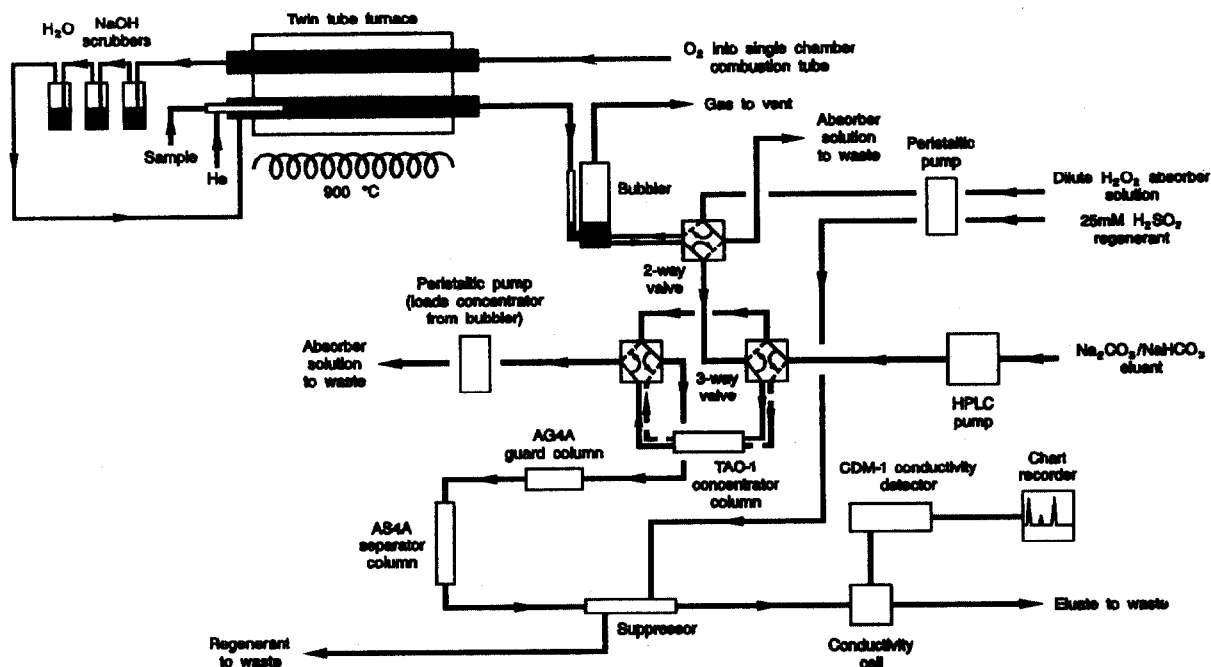


Fig. 1. Schematic diagram of the C-IC apparatus. Not drawn to scale. See Experimental section for details.

urities that may be present. The last Dreschel bottle contains 50 ml of conductivity water to remove any residual NaOH carried over from the first two scrubbers. This purification stage is essential in order to reduce the gas blanks to a manageable level.

The purified oxygen is then fed into the outer chamber of the second combustion tube (H. Baumbach Ltd.). This tube consists of inner and outer silica sleeves (see Fig. 3). The sample is injected through a rubber septum into a helium gas carrier stream in the inner chamber of this combustion tube. Sample introduction is carried out via a syringe (Hamilton, 100  $\mu$ l, fitted with a 71 mm needle), mounted on a constant rate injector (Sage Instruments Model 341). The sample is volatilised in the helium stream and carried down the inner chamber where it passes through four slits. At this point the sample-helium mixture meets the purified oxygen in the outer chamber and combustion takes place. The combustion products are then swept into the interface module.

**Interface module.** This module links the combustion furnace to the ion chromatograph (see Fig. 3).

It consists of a glass bubbler containing a fixed volume of dilute hydrogen peroxide absorber solution through which the exit gases from the combustion tube are vented to atmosphere. The peroxide solution is introduced into the bubbler by a peristaltic pump (Ismatec MP13) fitted with 2.79 mm purple/white silicon tubing, via a PTFE two-way rotary valve (Rheodyne Type 50). Whilst the sample is being combusted the bubbler is connected to the back end of the sample combustion tube by a ball and socket joint and held in place by a spring clip. A low-voltage heating tape (Electrothermal Engineering), maintained at 60°C via a variable voltage transformer (Zenith Instruments), is wound around the delivery arm of the bubbler to avoid "cold spots" and consequent condensation problems.

**The chromatography module.** This module is essentially made of components manufactured by Dionex (see Figs. 1 and 2) and plumbed with 1/16 in. I.D. tubing (1 in. = 2.54 cm) throughout. A three-way, air-activated valve (Dionex P/N 035913) is used to control the flow of sample and eluent during the loading and injection operations. When

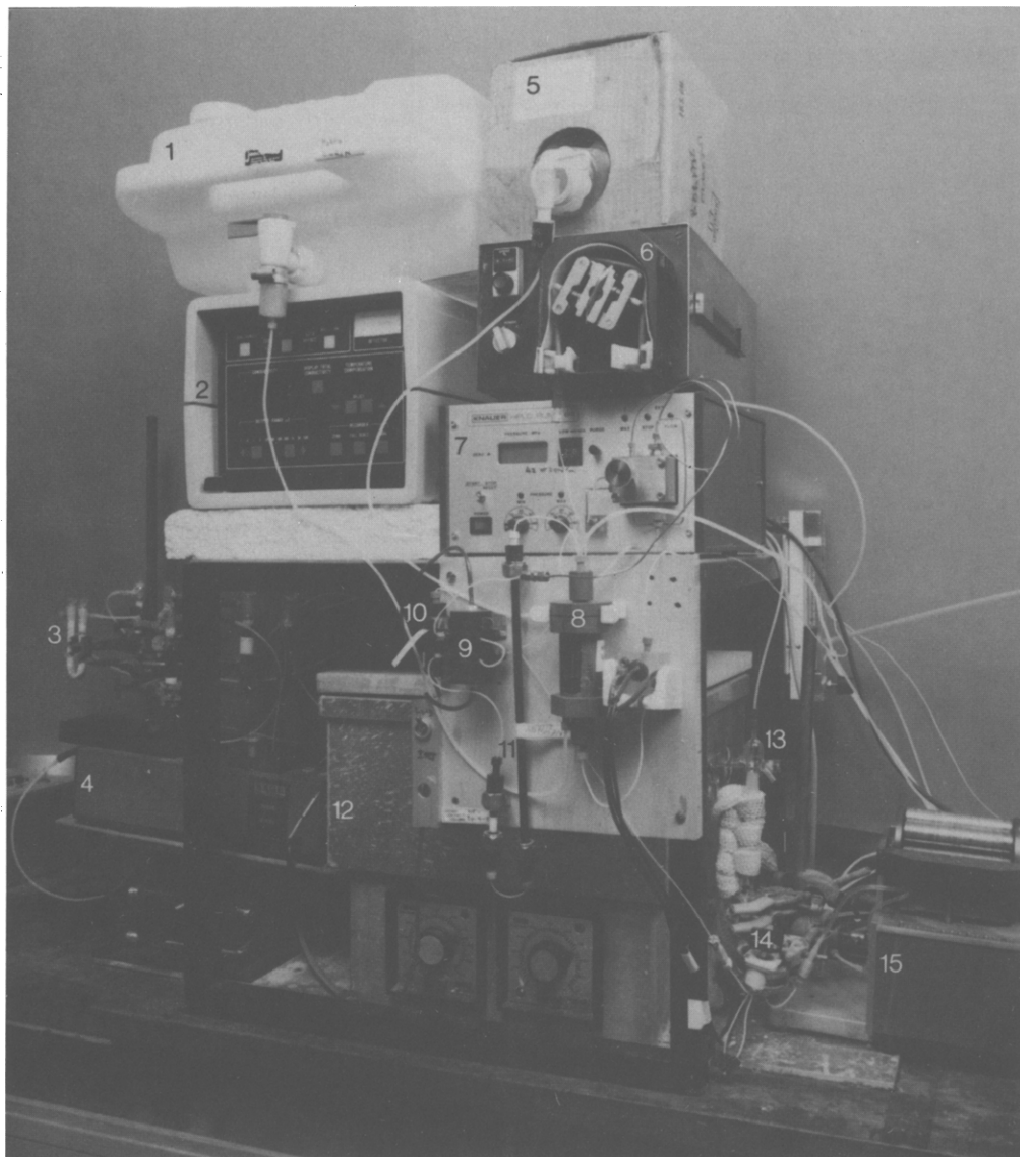
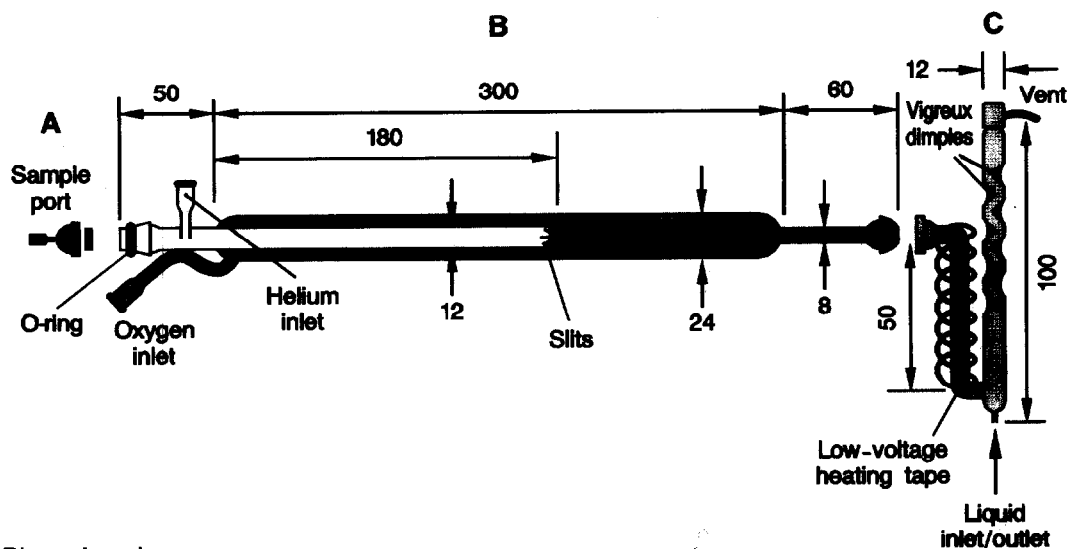


Fig. 2. Photograph of the C-IC analyser Mk I. 1 = Regenerant housing; 2 = conductivity detector; 3 = NaOH and solid scrubbers (the solid scrubbers were later removed); 4 = syringe drive; 5 = eluent housing; 6 = peristaltic pump (Watson-Marlow); 7 = HPLC pump; 8 = fibre suppressor; 9 = 3-way valve; 10 = concentrator column; 11 = IC columns; 12 = twin combustion furnace, housing the two combustion tubes; 13 = bubbler; 14 = 2-way valve; 15 = peristaltic pump (Ismatec). For further details see Experimental section.

the valve is switched to the “load” position the absorber solution containing the acidic combustion products is drawn, by a peristaltic pump (Watson-Marlow 202U) fitted with marprene tubing, through a Dionex TAC-1 concentrator column. When switched to the “inject” position, the concen-

trator column is flushed with eluent pumped through the system by an HPLC pump (Knauer Type 64). The anions of interest are separated from each other and interfering species by ion (exchange) chromatography using Dionex AG4A and AS4A guard and separator columns, and detected by con-



#### Dimensions in mm

Fig. 3. (A) Injection port, (B) combustion tube and (C) bubbler used in the C-IC analysis. Individual units are drawn to scale, but the bubbler scale is different to that of the combustion tube.

ductivity using a Dionex CDM-1 conductivity detector and cell after chemical suppression of the eluent [29] using a Dionex Fibre Suppressor (P/N 035691). Dilute sulphuric acid regenerant is pumped through the suppressor column at a constant rate via the Ismatec MP13 peristaltic pump. The chromatograms are recorded on a chart recorder (Servogor 120) and the heights measured manually.

#### Reagents

All reagents were AnalaR grade purchased from BDH and used as received, unless otherwise stated.

**Conductivity water.**  $<0.06 \mu\text{S}/\text{cm}$ . Freshly distilled and deionised using a water purifier (Millipore, Milli-Q system).

**Organic solvents.** Xylene, low in sulphur (SLR grade, Fisons), decalin (decahydronaphthalene) (GPR grade), isooctane (2,2,4-trimethylpentane) (ASTM reference grade, Hatterman Fuels), *n*-hexadecane (GPR grade), propan-2-ol (IPA), acetone and toluene.

**Standard materials.** Dibutyl sulphide,  $[(\text{CH}_3(\text{CH}_2)_3)_2\text{S}]$ , (Aldrich), chlorobenzene ( $\text{C}_6\text{H}_5\text{Cl}$ ), 1-chloro-2,4-dinitrobenzene [ $\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2$ ], (Microanalytical reagent, Hopkin & Williams), S-benzyl-thiuronium chloride [ $\text{C}_6\text{H}_5\text{CH}_2-$

$\text{S}-\text{C}(:\text{NH})-\text{NH}_2 \cdot \text{HCl}$ ], (Microanalytical reagent grade), sodium chloride, (Aristar grade) and sodium sulphate, anhydrous powder.

**C-IC reagents.** Sodium hydroxide solution (50%, w/v), sulphuric acid (sp. gr. 1.84), hydrogen peroxide, 100 vol (Aristar grade), sodium carbonate, (Aristar grade) and sodium hydrogen carbonate.

**Gases.** Oxygen (BOC), helium, ultrapure grade (G & E Union Carbide).

#### Preparation of reagent and standard solutions

Conductivity water was used in the preparation of all eluents and aqueous reagents and standards.

**IC Eluent.** 2.0 mM  $\text{Na}_2\text{CO}_3$ , 0.75 mM  $\text{NaHCO}_3$  was prepared in 4-l batches by dilution of eluent concentrates of 1 M  $\text{Na}_2\text{CO}_3$  and 1 M  $\text{NaHCO}_3$ .

**Regenerant.** 12.5 mM  $\text{H}_2\text{SO}_4$ , prepared by diluting 5.6 ml of the conc. acid to 8 l.

**Absorber solution.** 0.02 vol  $\text{H}_2\text{O}_2$ , prepared in 4-l batches by dilution of the 100 vol  $\text{H}_2\text{O}_2$ .

**Scrubber solution.** 50% NaOH solution, as purchased.

**Inorganic standards.** Stock solutions (100 ml) of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  (1000 mg/l) were prepared after drying the NaCl at  $150^\circ\text{C}$  for 2 h, and the  $\text{Na}_2\text{SO}_4$  at  $105^\circ\text{C}$  for 1 h.

**Organic standards.** Stock solutions (100 ml) con-

taining *ca.* 600 mg/l Cl were prepared accurately by dissolving known masses of chlorobenzene and 1-chloro-2,4-dinitrobenzene in toluene. Similarly a stock solution containing *ca.* 600 mg/l S was prepared by dissolving dibutyl sulphide in isooctane, and a mixed standard containing *ca.* 300 mg/l of Cl and S by dissolving S-benzyl-thiuronium chloride in propan-2-ol. Calibration standards were freshly prepared as required by dilution of the stock solutions with the appropriate solvent, and discarded after five days.

All organic standards, the eluent concentrates and the 100 vol H<sub>2</sub>O<sub>2</sub> were stored in a refrigerator at 4 ± 1°C.

#### *Analytical conditions*

Sample injection volume, 50–100 µl; sample injection rate, *ca.* 20 µl/min; helium flow-rate, 40 ml/min; oxygen flow-rate, 160 ml/min; absorber solution volume, *ca.* 1.5 ml (wash volume, *ca.* 1.5 ml); eluent flow-rate, 2 ml/min; suppressor regenerant flow-rate, 2 ml/min.

#### *Operation of the C-IC analyser*

The sample is injected into the inner sleeve of the combustion tube via a syringe held in a constant-rate injector. The syringe is positioned so that the needle tip protrudes approximately 60 mm into the inner chamber of the combustion tube, *i.e.* approximately 10 mm past the furnace entrance. The sample volatilises in a helium carrier stream and passes through four slits into the outer chamber where it combusts on contact with purified oxygen. The combustion products (H<sub>2</sub>O, CO<sub>2</sub>, HCl, SO<sub>2</sub>, SO<sub>3</sub>, NO, HBr, etc.) are carried into the bubbler where the water-soluble compounds are scrubbed from the gas stream by the dilute peroxide. The dilute peroxide ensures that all the combustion products of organic sulphur are converted to sulphate.

When all the sample has been combusted (normally 2.5–5 min), the bubbler is disconnected from the combustion tube (by removing the spring clip), and its contents loaded into the concentrator column by turning on the second (Watson-Marlow) peristaltic pump, with the Dionex valve switched to the load position. Provided its capacity is not exceeded, the concentrator column collects all the

anionic species whilst the excess peroxide solution is pumped through the concentrator to waste. When this operation is complete a further aliquot of peroxide solution is pumped into the bubbler via the Rheodyne two-way switching valve. The bubbler is then reconnected to the combustion tube for 15 s so that the gas flow through the absorber solution effectively “washes” the walls of the bubbler. This aliquot is also pumped onto the concentrator column.

Once loading of the second aliquot (wash) of peroxide has been completed, the air-activated valve is switched to the “inject” position in order to direct eluent through the concentrator column. The eluent displaces the anions from the concentrator onto the main column where the ions of interest are separated from each other and interfering species, and detected as the acids by conductivity after chemical suppression of the eluent. The chromatograms are recorded on a chart recorder and the peak heights used for quantification. Correction for any contribution from the gases and absorber solution is made by repeating the above operations but without injecting any sample, *i.e.* allowing the gases to bubble through the absorber solution for the same time as that for the samples.

The total analysis time using typical sample injection volumes of 50 µl and an injection rate of 20 µl/min can be calculated from the formula  $12n - 3$ , where  $n$  (the number of analyses) is greater than 1. Each analysis takes approximately 12 min, but loading of each subsequent sample onto the concentrator column may be performed whilst the preceding sample is still eluting from the main column, since the time for combustion is never shorter than the time required for a sample to elute from the concentrator. For analysis at levels below 0.1 mg/l where larger volumes of sample may be combusted, total analysis time will increase in accordance with the time taken for combustion.

#### *Microcoulometry*

Sulphur determinations were carried on a Dohrmann MCTS-130 using conditions laid down in ref. 9. Chlorine determinations were carried out on a Dohrmann MCTS-120 using conditions laid down in ref. 10.

TABLE I

## CHARACTERISTICS OF VARIOUS COMBUSTION METHODS FOR ELEMENTAL ANALYSIS BY IC

	Oxygen flask	Oxygen bomb	Wickbold
Sample size	20 mg	0.5 g	30 g
Final absorber volume (ml)	5	10	100
Sample type	Solids Non-volatile liquids	Solids Liquids	Liquids Gases
Detection limit (mg/kg), Cl	100	10	< 0.5
S	50	5	< 0.5

## DEVELOPMENT OF THE C-IC ANALYSER

Previous studies [11] had indicated that C-IC had the potential for analyses at sub ppm (w/w) level provided the sample combustion products could be collected in a volume of absorber solution small enough to be loaded onto a concentrator column. Oxygen flask [30,31] and oxygen bomb [32] methods were limited by either the sample mass combusted or the volume of absorber required. Wickbold combustions employing an oxyhydrogen burner [33] were compatible with sub-ppm (w/w) analysis (Table I) but required a large sample mass (*ca.* 30 g). From these studies it was concluded that none of these combustion methods was suitable for interfacing with an IC module and that a tube furnace combustion would be both compatible with interfacing and the safest way of burning the samples.

The development of the C-IC analyser from the initial concept to the point at which it could be used routinely for "real" samples (Mk I Model, Fig. 2) occurred over a two-year period. A number of significant changes and refinements to the original designs and procedures were made.

*Purification of the oxygen supply*

The success of the analyser is critically dependent on establishing a consistent, low blank. The blank is made up of any entities which ultimately contribute to the species of interest *i.e.* chloride and sulphate ions. In the early development stages, it was apparent that the chloride blank was extremely variable and significant in analyses at levels of *ca.* 5 mg/l. A very small sulphate blank was also observed at these levels but was found to be consistent. The extent of the chloride blank was a source of concern

because it had the potential to limit both the LOD and repeatability of the method. The principal source of the chloride blank was found to be the oxygen supply, probably due to contamination from traces of chlorinated solvent associated with degreasing agents used to clean the hard-plumbed gas lines from the cylinder bays outside the building. For this reason, a clean-up procedure for the oxygen supply was implemented. Thus, the original single furnace was replaced by a twin furnace to allow the oxygen to be purified as described earlier. Solid scrubbers containing soda lime and charcoal (situated between the combustion tube and NaOH scrubbers) were also tried, but these were discarded since, when saturated, they were found to contribute to the blank. The ultrapure helium was found to be free of organo-chlorine and organo-sulphur so this was used without further purification.

*Bubbler design*

Another key area of development for the analyser was the design of the glass bubbler. Original feasibility studies were carried out using a bubbler fitted with a tap (Fig. 4a). This allowed the absorber solution to be drained from the bubbler and manually injected onto the concentrator column. Once suitable combustion conditions were established, a bubbler design was required that had the capacity to be disconnected from the combustion tube after each analysis (to keep the blanks down to a minimum), and an end fitting that would accommodate loading of the concentrator column directly. Early prototypes had straight internal surfaces, no capillary feed and were open to the atmosphere (Fig. 4b). The side arm was fitted with a heating tape (controlled at 60°C) to avoid any problems with

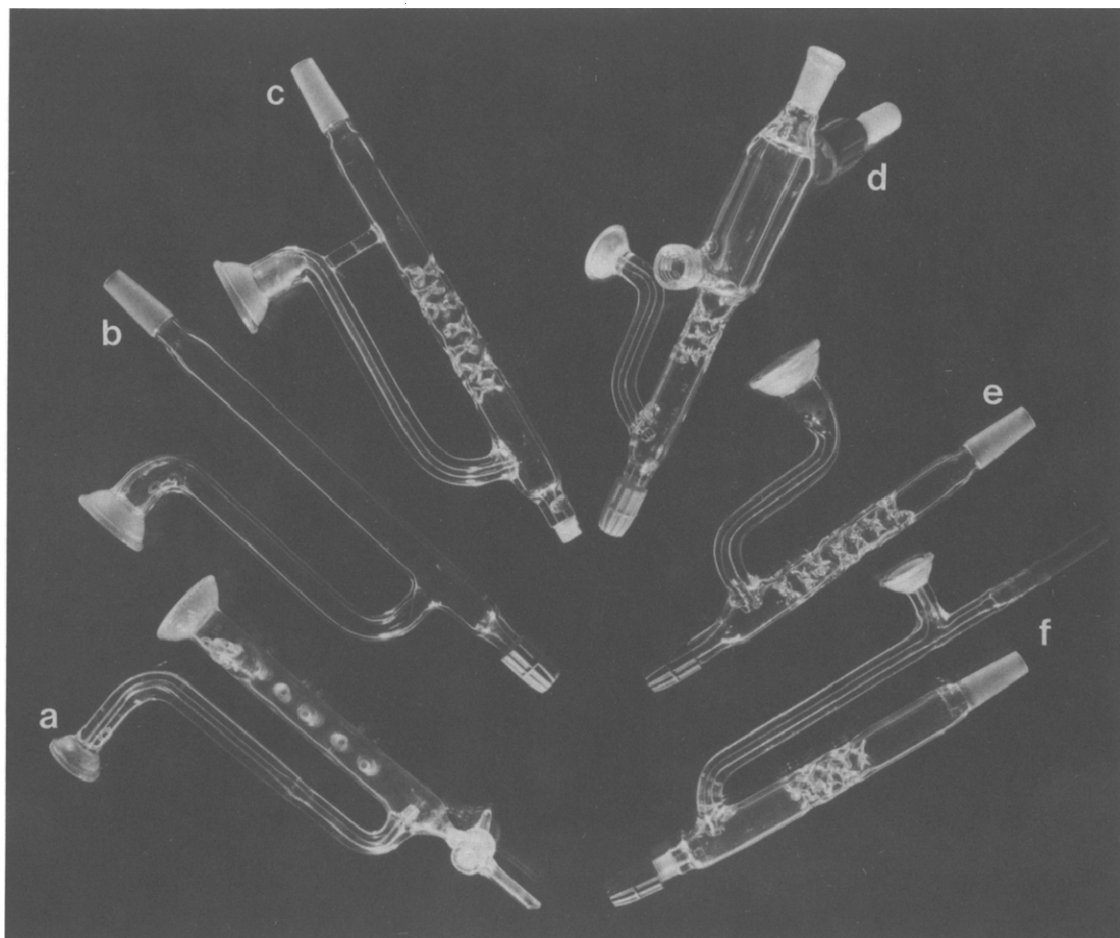


Fig. 4. Development of the bubbler. (a) Original bubbler with tap fitting; (b) straight bubbler, no capillary; (c) long sidearm, capillary and vigreux-type dimples; (d) short sidearm and condenser; (e) short sidearm, extra vigreux dimples, no condenser; (f) bubbler with metal attachment on the sidearm to accommodate an ozone stream for simultaneous Cl, S and N analysis.

condensation of combustion products. Although these prototypes worked fairly well, recoveries were variable due to loss of absorber through the top of the bubbler. This was overcome by introducing a capillary into the sidearm, and adding “Vigreux-type dimples” to the internal walls to break up the bubbles (Fig. 4c). At one stage a condenser was also fitted onto the bubbler (Fig. 4d) but this was found to have no advantage. Finally the size of the bubbler was reduced, extra Vigreux dimples introduced and the length of the sidearm reduced in proportion to the bubbler (Fig. 4e).

#### *On-line absorber supply*

During the original studies the  $\text{H}_2\text{O}_2$  solution

was added manually via pipette. The new designs allowed the bubbler to be filled via a valve and peristaltic pump. This reduced the possibility of contaminating the absorber solution.

#### *Procedural changes*

Apart from the oxygen supply, other possible sources of sulphur and chlorine contaminants are the solvents used in the preparation of standards (ASTM-grade isooctane was found to contain  $<0.03 \mu\text{g}/\text{ml}$  chlorine), the absorber solution and the operator. The use of a regimented procedure in making up standards and operating the instrument, including taking care to dispense the same volume of absorber (and wash) for each analysis, discon-



necting the bubbler from the column as soon as each combustion was complete, and wearing gloves to prevent post-combustion contamination with inorganic salts ( $\text{Cl}^-$  in skin), resulted in consistent, low blanks.

It was also noticed that at the start of the day, the initial blanks from washing the bubbler were very high and contained up to six peaks. This was thought to be due to contamination from the laboratory atmosphere. This contamination was greatly reduced by adding a cap (with vent) (Fig. 3) to the bubbler, and leaving the bubbler full of deionised water when not in use.

## RESULTS AND DISCUSSION

### Operating conditions

The combustion conditions were optimised by setting the helium flow-rate as recommended in [10] and adjusting the oxygen flow-rate so that no loss from the bubbler was evident and complete combustion of standards in isooctane was observed when the sample injection rate was set at 20  $\mu\text{l}/\text{min}$ . This optimum flow-rate, based on observation rather than experimental data, was found to be 160 ml/min. At lower oxygen flow-rates, incomplete combustion could be observed by the deposition of carbon in the bubbler. At higher flow-rates, loss of the absorber solution from the top of the bubbler was observed. Volatilising the sample in a carrier stream of helium rather than injecting directly into a stream of oxygen allows a faster injection rate, which is a critical factor in determining both the analysis time and, more importantly, the blank level.

Since standard IC conditions recommended by the manufacturer were used, further optimisation experiments were deemed unnecessary.

### Blank values

High, inconsistent blanks render the analyser inoperable at trace levels. However, using the purification stages and procedures described earlier, consistent, low blanks were attained (Table II), enabling trace analysis at levels down to 0.03 mg/l.

### Concentrator column capacity

The capacity of the concentrator column is important when traces of one element are to be deter-

TABLE II  
TYPICAL BLANK DATA

Peak heights obtained after the combustion of 50  $\mu\text{l}$  isooctane combusted under the normal CIC conditions listed in the Experimental section. Sensitivity set at a full scale detection (FSD) of 3  $\mu\text{S}$ .

	Chlorine	Sulphur
$\bar{x}$	35.3	7.6
$\sigma_{n-1}$	3.30	1.6
$2\sigma_{n-1}$	6.60	3.30
Detection limit (mg/l) <sup>a</sup>	0.022	0.030

<sup>a</sup> Detection limits calculated from  $2\sigma_{n-1}$  and the heights obtained for standard calibrations of 1-chloro-2,4-dinitrobenzene and dibutyl sulphide in isooctane, using 50- $\mu\text{l}$  injection volumes.

mined in the presence of much higher concentrations of another element.

Using inorganic standards made up in absorber solution, the capacity of the TAC-1 concentrator column was found to be in excess of 100  $\mu\text{g}$  for sulphate (33  $\mu\text{g}$  sulphur) and 50  $\mu\text{g}$  for chloride. These capacities were found to decrease by just over 50% over a period of 6 months.

For a mixture containing sulphate and chloride ions, the column capacity for chloride is limited by the sulphate concentration, since sulphate has a greater affinity for the resin and displaces chloride if no free sites are available. At the loading rate used in the C-IC analyser, loss of chloride at the 0.05  $\mu\text{g}$  level was observed when the sulphate exceeded 75  $\mu\text{g}$ . Studies of capacity with organic standards in isooctane (injection volume 50  $\mu\text{l}$ ) were in good agreement with the inorganic studies. It was shown that no loss of organic chlorine at the 1 mg/l level (0.05  $\mu\text{g}$  Cl) was observed until the concentration of sulphur exceeded 520 mg/l (26  $\mu\text{g}$  S, equivalent to 78  $\mu\text{g}$  sulphate). These studies showed that chloride was displaced by sulphate prior to complete saturation, indicating that another factor is involved. It was thought that a lower loading rate may increase the level of sulphate at which chloride is lost, but this was not tried since this would increase the time of analysis and was not particularly relevant since the analyser was being developed for trace level applications.

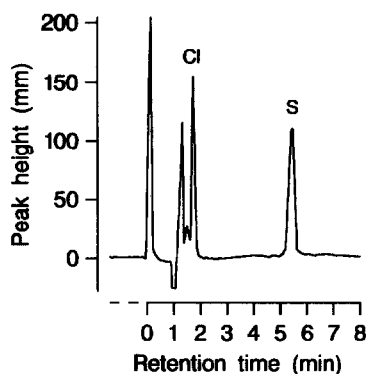


Fig. 5. IC separation of elemental chlorine and sulphur after combustion and conversion to chloride and sulphate. Standard concentrations, 0.4 mg/l Cl (chlorobenzene) and 1.0 mg/l S (dibutyl sulphide) in isooctane. Injection volume, 50  $\mu$ l at 20  $\mu$ l/min. Other conditions as described under analytical conditions in the Experimental section.

These studies showed that the absolute capacity of the concentrator column depends on its age and condition, whilst the efficiency of the retention process for a particular species is dependent on both the interference effects of other ions and the loading rate.

#### Recoveries

The recovery of chlorine and sulphur is effectively a measure of the efficiency of the sample combus-

tion, the trapping of the combustion products in the absorber solution and the retention of the subsequent anions on the concentrator column. As all the sulphur and chlorine species formed in combustion are converted in the peroxide absorber solution to sulphate and chloride respectively, it was possible to directly compare peak heights (blank corrected) from combustion of organic standards with those associated with direct injection of inorganic standards onto the concentrator column. A typical chromatogram obtained for a mixed organic standard after combustion is shown in Fig. 5. This chromatogram differs from that obtained by direct injection of inorganic standards, in that formate and acetate peaks, directly between the water dip and chloride peaks, are often observed. These peaks are due to incomplete combustion of the organic matrix. However, this does not appear to affect adversely the recovery of chlorine and sulphur.

From the data shown in Table III it can be seen that at the 2 mg/l level the recoveries for Cl and S were greater than 94% for injection volumes ranging from 10–50  $\mu$ l (0.02–0.1  $\mu$ g). The matrix and sample type appeared to have little or no effect on recovery. Table IV shows that at the 2 mg/l level, recoveries for various standards of chlorobenzene, 1-chloro-2,4-dinitrobenzene, benzyl-thiuronium chloride and dibutyl sulphide in a range of solvents, were always greater than 93%.

TABLE III

#### RECOVERY OF S AND Cl AT THE 2 mg/l LEVEL FOR VARIOUS SAMPLE INJECTION VOLUMES

Various volumes of organic standards of chlorobenzene (Cl = 2 mg/l) and dibutyl sulphide (S = 2 mg/l) in isooctane were analysed by C-IC (using the analytical conditions described in the Experimental section) and the peak heights (blank corrected) directly compared to those obtained for inorganic standards prepared from NaCl (Cl = 2 mg/l) and Na<sub>2</sub>SO<sub>4</sub> (SO<sub>4</sub><sup>2-</sup> = 6 mg/l) and analysed directly by IC by injecting onto the concentrator column. All peak heights are means of three analyses and quoted in mm. FSD for Cl heights = 10  $\mu$ S, FSD for S heights = 3  $\mu$ S.

Injection volume (ml)	Chlorine			Sulphur		
	Inorganic	Organic	Recovery (%)	Inorganic	Organic	Recovery (%)
10	33	31	94	40	38	95
20	67	64	96	86	84	98
30	103	100	97	130	127	98
40	139	136	98	176	172	98
50	175	177	101	223	226	101

TABLE IV

## RECOVERY OF ORGANIC Cl AND S IN VARIOUS SOLVENT MATRICES

Organic standards with Cl and S concentrations of 2 mg/l were prepared by dissolving chlorobenzene and butyl sulphide in toluene, xylene, decalin and hexadecane; 1-chloro-2,4-dinitrobenzene and butyl sulphide in isooctane, and S-benzyl-thiuronium chloride in propan-2-ol (Cl = 2 mg/l, S = 1.8 mg/l). Recoveries calculated by direct comparison of the peak heights (blank corrected) obtained from C-IC analysis (using analytical conditions described in Experimental section) with those obtained from direct IC analysis of inorganic standards ( $\text{Cl}^- = 2 \text{ mg/l}$ ,  $\text{SO}_4^{2-} = 6 \text{ mg/l}$ ).

Solvent	Recovery (%)	
	Chlorine	Sulphur
Toluene	98.4	—
Isooctane	101.0	101.0
Xylene	100.8	96.3
Decalin	95.1	99.1
Hexadecane	93.1	98.0
Propan-2-ol	99.2	98.7

*Linearity and repeatability*

Calibrations with mixed standards of 1-chloro-2,4-dinitrobenzene and dibutyl sulphide in isooctane showed that over the trace level range (0–3 mg/l) the detector response expressed as peak height was rectilinear for both chlorine ( $r = 0.9997$ ,  $n = 8$ ) and sulphur ( $r = 0.9994$ ,  $n = 9$ ) (Fig. 6). Similar linearity (Cl,  $r = 0.9996$ ,  $n = 5$ ; S,  $r = 0.9995$ ,  $n = 6$ ) was observed using individual standards of chlorobenzene (Cl conc. range, 0–0.6 mg/l) and dibutyl sulphide (S conc. range 0–1.0 mg/l) in xylene (Fig. 7).

It was noticed that for the C-IC analyses the day-to-day variation in peak heights and the peak height ratios  $\text{Cl}^-:\text{SO}_4^{2-}$  varied much more than in aqueous IC using a sample loop injection. This may have been caused by small changes in eluent composition and the condition of the concentrator, guard and separator columns. However, this variation did not affect recoveries or repeatability. The practice of preparing the eluent by dilution of eluent concentrates reduced this variation but a daily calibration was still required.

Repeatability studies were carried out for both Cl and S using standards of chlorobenzene and dibutyl

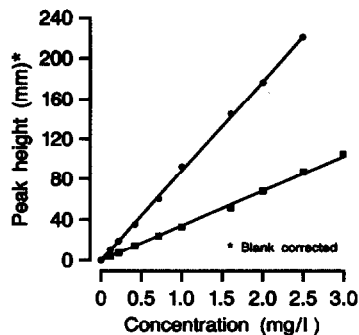


Fig. 6. Calibration curves for Cl (●) and S (■) in the range 0–3 mg/l after combusting mixed standards of 1-chloro-2,4-dinitrobenzene and dibutyl sulphide in isooctane. Sensitivity set at an FSD of 10  $\mu\text{S}$ .

sulphide in isooctane. From Table V it can be seen that for Cl at the 0.4 mg/l and 0.05 mg/l levels the standard deviation ( $n = 10$ ) was found to be 2.9 and 9.9%, respectively. For S, the % standard deviation was found to be 3.5 and 6.9%, at the 0.5 mg/l and 0.1 mg/l levels, respectively.

*Comparison with microcoulometry*

Good agreement between the C-IC method and the established technique of microcoulometry [34] was obtained for Cl and S standards in isooctane (conc. range 0.5–50 mg/l) (Table VI), and samples of crude oil distillates and reformer feedstocks (Table VII). However, the repeatability of the C-IC method was found to be superior to that of microcoulometry, especially at levels of less than 0.4 mg/l.

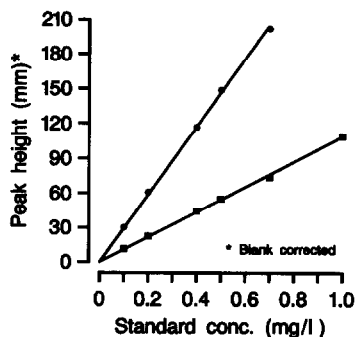


Fig. 7. Calibration curves for Cl (0–0.6 mg/l) (●) and S (0–1.0 mg/l) (■) obtained from the combustion of individual standards of chlorobenzene and dibutyl sulphide in xylene. Sensitivity set at an FSD of 3  $\mu\text{S}$ .

TABLE V

REPEATABILITY DATA ( $n = 10$ ) FOR THE DETERMINATION OF SULPHUR AND CHLORINE BY C-IC

Standards of chlorobenzene and dibutyl sulphide in isooctane, injection volume 50  $\mu$ l. Analytical conditions as described in Experimental section.

	Chlorine		Sulphur	
	0.40 mg/l	0.05 mg/l	0.50 mg/l	0.10 mg/l
Sensitivity setting ( $\mu$ S)	3	1	3	1
Peak heights (mm)	120	49	54	33
(blank corrected)	126	53	51	37
	118	48	57	35
	124	41	56	41
	123	41	55	39
	128	44	59	34
	124	43	55	36
	124	40	60	35
	126	41	57	34
	117	48	55	35
$\bar{x}$ (mean height, mm)	123	44.8	56.6	35.9
$\sigma_{n-1}$	3.6	4.42	1.96	2.47
$2\sigma_{n-1}$	7.2	8.84	3.92	4.94
$\bar{x}$ (mg/l) <sup>a</sup>	0.41	0.050	0.51	0.109
$2\sigma_{n-1}$ (mg/l)	$\pm 0.024$	$\pm 0.010$	$\pm 0.036$	$\pm 0.015$

<sup>a</sup> Calculated from calibration curve obtained for inorganic standards.

A comparison of S results by C-IC with those obtained by inductively coupled plasma-optical emission (ICP) for a series of catalyst samples in different solvents is shown in Table VIII. As most of

these samples contained much higher levels of S, dilution with the appropriate solvent prior to analysis was carried out. With one exception all the results agreed to within 6.4%.

TABLE VI

## COMPARATIVE DATA: C-IC VERSUS MICROCOULOMETRY —STANDARDS

A series of standards of chlorobenzene in xylene and dibutyl sulphide in isooctane were analysed by C-IC (using the analytical conditions in the Experimental section) and microcoulometry (using the analytical conditions and procedures laid down in refs. 9 and 10).

Standard concentration	Chlorine (mg/l)		Sulphur (mg/l)	
	C-IC	Microcoulometry	C-IC	Microcoulometry
0.5	0.48	0.6	0.51	0.6
1.0	1.05	1.1	0.98	1.0
2.0	2.05	2.1	1.99	2.1
5.0	5.1	5.1	5.0	5.1
10.0	9.8	9.6	9.8	10.2
50.0	51	48	48	48

TABLE VII

## COMPARATIVE DATA: C-IC VERSUS MICROCOULOMETRY—SAMPLES

Crude oil distillates and reformer feedstocks were analysed by C-IC (using the analytical conditions described in the Experimental section) and microcoulometry (using the analytical conditions and procedure laid down in refs. 9 and 10). Quantification was carried out by reference to an external calibration with chlorobenzene and dibutyl sulphide in isoctane. Errors: At levels below 0.4 mg/l the error bar for microcoulometric results is  $\pm 0.05$  compared to  $\pm 0.02$  for C-IC results.

Sample	Chlorine (mg/l)		Sulphur (mg/l)	
	C-IC	Microcoulometry	C-IC	Microcoulometry
<i>Crude oil distillates (15–149°C)</i>				
Tapis blend	0.68	0.6		
Labuan	1.03	1.1		
Iranian heavy	0.42	0.5		
Iranian light	0.59	0.6		
<i>Reformer feeds</i>				
A	0.12	0.13		
B	0.29	0.25		
C	0.37	0.35		
D	0.41	0.40		
E			0.48	0.54
F			0.25	0.19
G			0.10	0.09

*Applications and scope*

Between 1988–1992, the C-IC analyser has been used to analyse over 900 samples. Originally the analyser was developed to analyse for Cl and S at sub-mg/l levels in reformer feeds and naphthas. However, due to demand and the lack of other suitable instrumentation the analyser was used to analyse other sample types. Crude oil distillates, C<sub>4</sub>–C<sub>10</sub> aromatics, gasolines, dimates and ethyl benzene have all been analysed for chlorine, whilst sulphur in toluene, C<sub>5</sub>/C<sub>6</sub> hydrocarbons, reformate aromatics, North Sea condensates, decane, methanol, hexane, jet fuel, 2-ethylhexanol and propan-2-ol has been determined. Such analyses have not been achieved without problems. Firstly, the more refractory samples can block the syringe. Secondly, whilst the analysis of samples with high levels (< 50 mg/l) of S and/or Cl is operationally very simple, since blank contributions at this level are negligible, subsequent trace level determinations can sometimes prove difficult, due to carry over from the combustion tube. Analysis at ultra-trace levels is best performed with a dedicated combustion tube and bubbler.

## RECENT DEVELOPMENTS AND FUTURE WORK

The Mk I Analyser has also been successfully used to determine nitrogen and bromine in organic

TABLE VIII

## COMPARATIVE DATA: C-IC VERSUS ICP FOR S IN CATALYST SOLUTIONS

A series of catalyst solutions in various solvents were analysed for S by C-IC, using the analytical conditions described in the Experimental section, and diluting with the appropriate solvent where necessary (to give S concentrations in the range 20–30 mg/l). ICP analyses were carried out using a Spectroflame Model P optical emission spectrometer (Spectro Analytical Instruments) set at 182.04 nm, calibrated with matrix-matched standards. C-IC quantification was by reference to an external calibration of dibutyl sulphide in isoctane.

Solvent	C-IC (mg/l)	ICP (mg/l)
Water	25.3 $\pm$ 0.3	25
Water	128 $\pm$ 5	120
Water	185 $\pm$ 5	185
2-Ethylhexanol	317 $\pm$ 10	374
2-Ethylhexanol	530 $\pm$ 25	566
Hexane	147 $\pm$ 5	155

and aqueous media. For simultaneous nitrogen, sulphur and chlorine determinations a modified bubbler (Fig. 4f) was required to facilitate the introduction of ozone into the sidearm. As the combustion product of nitrogen under these conditions is nitrogen monoxide (NO) which is insoluble in water, an oxidation stage with ozone to form soluble nitrogen dioxide (NO<sub>2</sub>) was required. Recoveries for nitrogen were found to be 35% at best. If sulphur and chlorine are not required, nitrogen recovery could theoretically be improved to 100% by bubbling the combustion products through an acidic KMnO<sub>4</sub> solution and absorbing in dilute peroxide. However, this was not tried since trace nitrogen is more conveniently determined by a combustion–chemiluminescence method using commercially available equipment.

The determination of bromide has also been investigated briefly. Bromide recoveries, determined by combusting standards of cetyl pyridinium bromide in xylene under the same analytical conditions as for Cl and S and comparing the peak heights with those obtained for aqueous KBr standards analysed directly, were found to be greater than 98% at the 1 mg/l level. Excellent agreement with X-ray fluorescence (XRF) was obtained for a series of Br<sup>-</sup>-containing catalyst solutions in various solvents (Table IX). Obviously these analyses could now be carried out directly on the newly developed solvent compatible IC columns, but the same method could be applied to the determination of bromine.

Since the development of the Mk I Analyser, IC technology has improved and these advances have been incorporated into the C–IC analyser. Thus, the fibre suppressor has been replaced with an AMMS-II membrane suppressor, with the regenerant being supplied by a pressurised vessel, the columns have been updated and the chromatograms recorded by an AI-450 data collection station. Furthermore, a UV–Vis detector has been introduced in-line to accommodate analysis of UV-absorbing species and to help in the identification of unknown peaks.

The most recent work has been the development of a new “flow cell” interface which allows a constant flow of fresh absorber solution into the bubbler and continual loading of combustion products onto the concentrator. This flow cell is still being

TABLE IX

COMPARATIVE DATA: C–IC VERSUS XRF FOR Br<sup>-</sup> IN CATALYST SOLUTIONS

A series of catalyst solutions in various solvents were analysed for Br<sup>-</sup> by C–IC, using the analytical conditions described in the Experimental section, and diluting with the appropriate solvent where necessary (to give Br<sup>-</sup> concentrations in the range 1–10 mg/l). XRF analyses were carried out using a Philips PW1404 wavelength dispersive X-ray spectrophotometer, using standard analytical conditions. C–IC quantification was by reference to an external calibration of cetyl pyridinium bromide in xylene.

Solvent	C–IC (mg/l)	XRF (mg/l)
<i>m</i> -Xylene	< 0.6	< 2
Hexane	90 ± 5	80 ± 1
Propan-2-ol	1260 ± 15	1375 ± 5
Water	2.5 ± 0.2	4 ± 0.5
	66 ± 2	64 ± 1
	246 ± 5	238 ± 1
	246 ± 5	246 ± 1
	253 ± 5	250 ± 1
	245 ± 5	244 ± 1

evaluated. Future studies will include the application of post column reactions to improve sensitivity and include other elements (*e.g.* thorium and xylene orange to determine fluorine), extending the scope of the analyser to facilitate the analysis of solid samples, and the automation of the analyser.

## CONCLUSIONS

The C–IC analyser described here can be used to determine sulphur and chlorine in liquid hydrocarbons at levels down to 0.03 mg/l, with the potential for measurements at single ng/ml levels. Results obtained are in good agreement with those obtained by conventional microcoulometric techniques. The simultaneous nature, speed and sensitivity of the analysis, gives the C–IC method several advantages over microcoulometry. The analyser has the potential for multi-elemental analysis and has the scope for adaptation to accommodate solid sample analysis.

## ACKNOWLEDGEMENTS

The authors wish to thank Dr. H. W. Handley for permission to discuss the new flow cell, Mr. M.

S. Jones for carrying out the ICP analysis, and Mr. T. Jervis and Mr. M. Townsend for making the bubblers and other specialised glassware.

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