

Note

Chromatographic analysis of alkali chlorine cell gas

S. K. DANG, P. D. GROVER and S. L. CHAWLA

Indian Institute of Technology, New Delhi-110029 (India)

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The analysis of alkali chlorine cell gas is important in keeping the amount of hydrogen at the anode below the explosion limit (3%) and in determining the current efficiency of the cells. Volumetric methods are inaccurate and time consuming for this purpose, whereas chromatographic methods have the advantage of suitability for on-line analysis.

Methods involving the use of katharometers alone for estimating the percentage of hydrogen or chlorine have been described¹⁻⁵ and since 1960 various attempts have been made to carry out the complete chromatographic analysis of the cell gas.

Neelay⁶ used two chromatographs with a manifold in the carrier-gas line connecting the two instruments. A combination of two columns in series was used as no single adsorbent separated all of the components. The first column, containing Fluorolube grease on Chromosorb, separated permanent gases, carbon dioxide and chlorine, while the second column, packed with molecular sieve 13X, separated hydrogen, oxygen, nitrogen and carbon monoxide. Carbon dioxide and chlorine, which are irreversibly adsorbed on molecular sieves, were diverted from this column through the manifold after their detection in the first instrument. Helium was used as the carrier gas. The concentration of hydrogen was determined using a thermal conductivity detector without column resolution. Lacy and Woolmington⁷ used a combination of silica gel and molecular sieve 5A columns for effecting separations. The silica gel column separated carbon dioxide and chlorine from each other and from permanent gases at temperatures above 50°, while the second column, containing molecular sieve 5A, separated hydrogen, oxygen and nitrogen. Argon or helium was used as the carrier gas. An on-stream gas chromatographic analysis was described by Martin⁸. Water, air and carbon dioxide were separated on a Porapak Q column using helium as the carrier gas and hydrogen, was determined by thermal conductivity measurements. Rutman *et al.*⁹ also used two columns in series for effecting the separations. The first column, containing 50% dibutyl phthalate on INZ-600 support, separated carbon dioxide and chlorine from permanent gases, while the second column, containing molecular sieve 13X, separated hydrogen, oxygen, nitrogen and carbon monoxide and adsorbed carbon dioxide and chlorine irreversibly. Argon was used as the carrier gas and the analysis was carried out at room temperature. These chromatographic methods require the use of expensive chromatographs and involve either argon or helium as the carrier gases, which are expensive and not always readily available.

In order to overcome these difficulties, a simple and inexpensive chromatographic system has been designed and fabricated for analysing alkali chlorine cell gas. The separation of the components is effected by using two chromatographic columns in series, with a thermal conductivity detector after each column. The first column contains silica gel and is used for separating carbon dioxide and chlorine from each other and from the permanent gases (oxygen and nitrogen), while the second column, containing molecular sieve 5A, separates oxygen, nitrogen and carbon monoxide. Hydrogen is used as the carrier gas. For the determination of hydrogen a separate injection is made in a stream of nitrogen carrier gas. In this step only one detector and the silica gel column operate and only hydrogen, carbon dioxide and chlorine are determined.

CHROMATOGRAPHIC APPARATUS AND RESULTS

The equipment used is shown in Fig. 1. The thermal conductivity detectors contain glass-coated bead thermistors as sensing elements enclosed in the symmetrical cavities of a hexagonal stainless-steel block. Each detector is incorporated in a separate Wheatstone bridge-type circuit. The outputs of the two detectors are recorded on a 5-mV potentiometric recorder. Under the operating conditions used the retention times of various components are such that only one recorder is required.

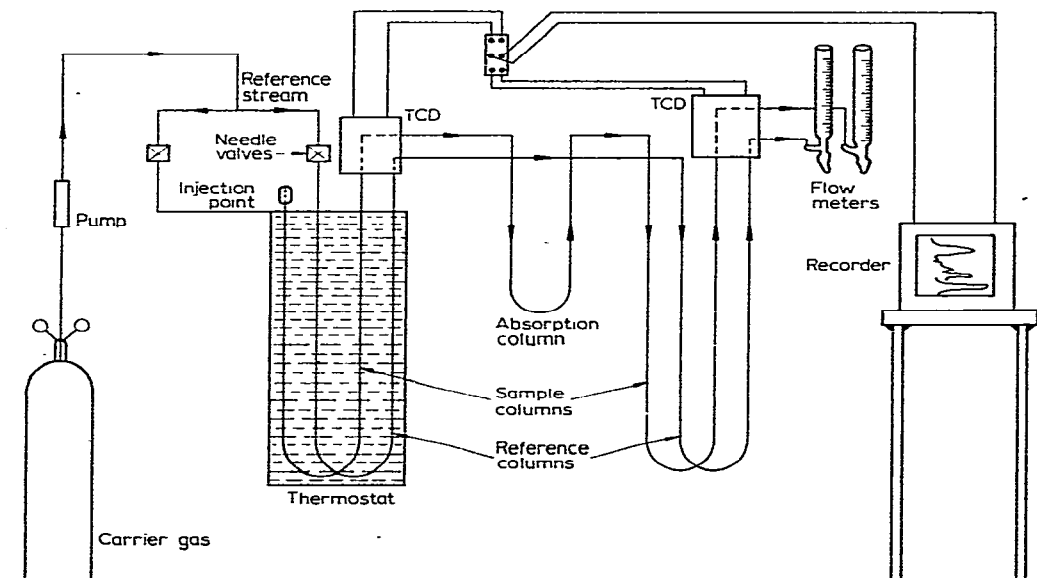


Fig. 1. Schematic diagram of the assembly.

The first column (glass tubing, 1950 × 6 mm I.D.) is packed with 50–72-mesh silica gel, previously dried at 110° for about 24 h, and is operated at 50–60°. This column is shielded from light by using black paper in order to avoid photochemical reaction of hydrogen and chlorine. The second column (glass tubing, 3750 × 6 mm

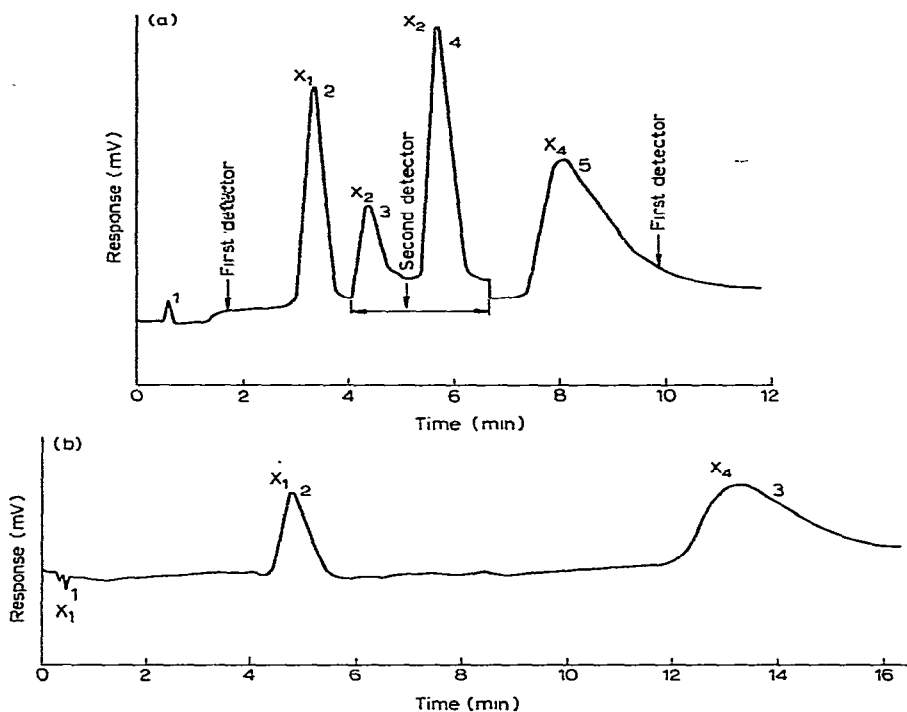


Fig. 2. Chromatograms of alkali chlorine cell gas. (a) Carrier gas hydrogen, both columns used. Peaks: 1 = air; 2 = carbon dioxide; 3 = oxygen; 4 = nitrogen; 5 = chlorine. (b) Carrier gas nitrogen, only silica gel column used. Peaks: 1 = hydrogen; 2 = carbon dioxide; 3 = chlorine. X_1 – X_4 , scale multiplying factors.

I.D.) contains 50–72-mesh molecular sieve 5A activated at about 400° for about 5–6 h and is operated at ambient temperature. Chlorine, which is irreversibly adsorbed on the molecular sieve, is removed after its detection in the first detector. For this purpose an intermediate column is used. This column (1100 × 15 mm I.D.) contains saturated potassium iodide and a small amount of starch impregnated on 10–30-mesh silica gel in one limb to remove chlorine; the other limb contains self-indicating reversible silica gel to absorb moisture arising from the iodide solution.

Hydrogen is used as the carrier gas instead of argon or helium because it is less expensive, gives larger signals and is readily available. A typical chromatogram obtained is shown in Fig. 2 and the retention times are given in Table I.

For the analysis of hydrogen in the cell gas, a separate injection is made in a

TABLE I
RETENTION TIMES OF COMPONENTS OF ALKALI CHLORINE CELL GAS

Sample No.	Component	Retention time (sec)	Resolving column
1	Air	29.5	Silica gel
2	Carbon dioxide	198	Silica gel
3	Oxygen	254	Molecular sieve
4	Nitrogen	340	Molecular sieve
5	Chlorine	486	Silica gel

stream of nitrogen carrier gas. Here only the silica gel column operates. The chromatogram is also shown in Fig. 2.

It can be seen from Fig. 2 that no peak was observed for carbon monoxide, which therefore was not present in the sample analysed, and no evidence for a hydrogen-chlorine reaction was observed as no peak due to hydrogen chloride was observed when either pure chlorine or the sample was injected.

Higher peaks were observed for oxygen, nitrogen and carbon dioxide present as impurities in chlorine. This result may be due to strong adsorption of chlorine by silica gel, which results in the concentration of the impurities in the carrier gas as the sample enters the column, probably due to occupation of active sites by chlorine. Similar effects were observed by Lacy and Woolmington⁷ during the analysis of alkali chlorine cell gas. Hence, for calibration purposes a standard mixture is used.

CONCLUSIONS

Compared with the cost of gas chromatographs described in the literature for the analysis of alkali chlorine cell gas (total Rs. 50,000 or US\$ 6600, provided one chromatograph is used), our equipment costs only Rs. 3500 (US\$ 500) plus the cost of a recorder (*i.e.* Rs. 12,000 or US\$ 1600).

The instrument gives very good performance, with good resolution. The sensitivity of the detectors is of the order of 0.56×10^2 mV·ml/mg. The lower limits of detection are reasonable, and amounts up to 0.016 ml of carbon dioxide and 0.021 ml of oxygen can be detected.

The proposed system is suitable for routine operation and can be connected directly to the sampling point in the plant for on-line analysis. A constant-volume sample loop will have to be interposed between the sampling point and the silica gel column for this purpose.

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