Journal of Chromatography, 147 (1978) 453–455
© Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 10,226

Note

Analysis of CO, CO_2, $COCl_2$, HCl and Cl_2 gas mixtures

A. BAIKER, H. GEISSER and W. RICHARZ

Swiss Federal Institute of Technology (ETH), Department of Industrial and Engineering Chemistry, 8092 Zürich (Switzerland)

(First received March 25th, 1977; revised manuscript received May 20th, 1977)

A mixture of carbon monoxide and chlorine is frequently used for the chlorination of metal oxides[1,2]. The products of this reaction are the corresponding metal chlorides and a mixture of waste gases, mainly CO, CO_2, $COCl_2$, HCl and Cl_2. Very few simple gas chromatographic (GC) methods for the analysis of such mixtures have been reported[3–5]. This paper describes the quantitative analysis of such gas mixtures by means of a simple one-column system.

EXPERIMENTAL

Reagents

The gases used had the specifications shown in Table I.

Apparatus

The apparatus consisted of a Gow-Mac Model 69-625 gas chromatograph fitted with a Gow-Mac Model 11-625 gas density detector. The PTFE column (9 m × 4.2 mm I.D.) contained 10% Arochlor 1232 on Chromosorb T, 40–60 mesh. The detector current was 285 mA and the detector temperature 165°. The column temperature was 32° and the pressure drop *ca.* 3 bar. The reference gas was helium, with a flow-rate of 630 ml/min; helium was also used as carrier gas, with a flow-rate of 200 ml/min.

The column was preconditioned at room temperature for 48 h with a N_2–H_2O stream flowing at 40 ml/min. At an inlet pressure of 3 bar the mole fraction of water was $8.3 \cdot 10^{-3}$.

TABLE I

SPECIFICATIONS OF GASES USED

Gas	*Purity (Vol. %)*	*Impurities*
He	> 99.996	N_2, O_2, Ar, H_2O
CO	> 99.99	N_2, O_2, Ar, H_2O
CO_2	> 99.9	N_2, O_2, Ar, H_2O
HCl	> 99.0	Cl_2 < 55 ppm
Cl_2	> 99.9	CO_2 < 500 ppm
$COCl_2$	> 99.9	HCl < 200 ppm

Preparation of gas mixtures

Gas mixtures were prepared in a glass vessel connected to a mercury manometer. The previously evacuated vessel was filled with each gas component to the desired partial pressure. Samples collected from the glass vessel always had a homogeneous composition. For each measurement 2.1 ml of the gas mixture was injected into the gas chromatograph by means of a gas sampling loop (Van de Craats model[6]).

RESULTS

A typical chromatogram of a mixture of the mentioned gases is given in Fig. 1. The corresponding retention times are shown in Table II. At 30° the preconditioned column kept its improved efficiency for several weeks. However, at higher temperatures we observed a gradual loss of the obtained effect owing to continuous desorption of water.

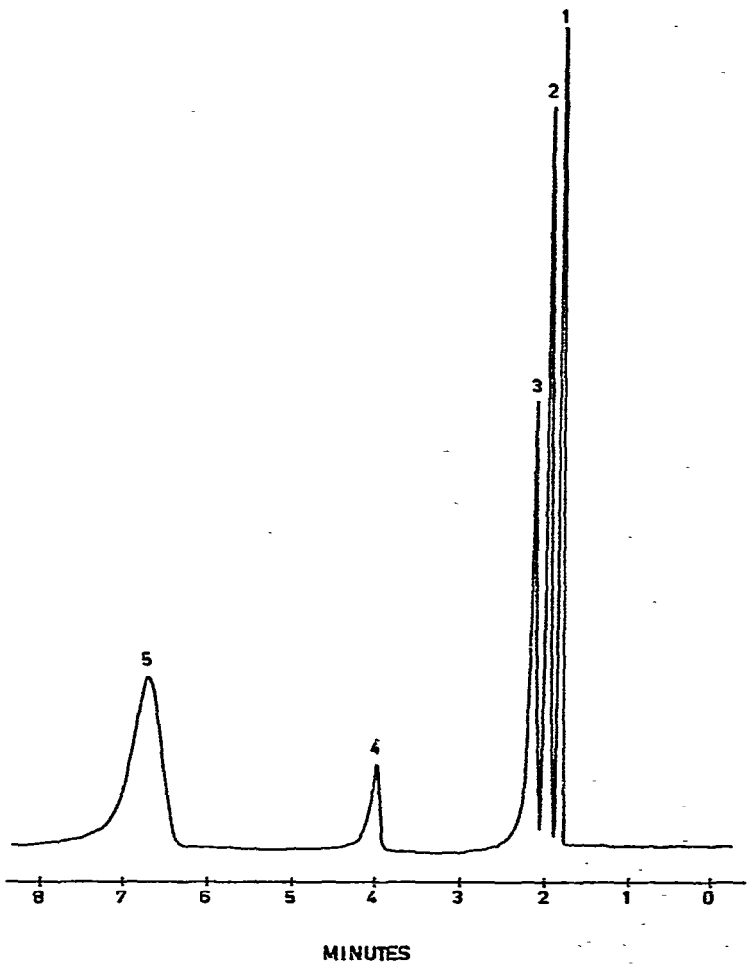

Fig. 1. Separation of the five-component mixture with preconditioned column.

TABLE II

MEASURED RETENTION TIMES (t_R)

*Peak no.**	*Compound*	t_R *(min)*
1	CO	1.7
2	CO_2	1.9
3	HCl	2.1
4	Cl_2	4.0
5	$COCl_2$	6.7

* *Cf.* Fig. 1.

CONCLUSION

A GC method was developed which permits the analysis of gas mixtures containing CO, CO_2, $COCl_2$, HCl and Cl_2 in a relatively short time. The analysis system consisted of a gas chromatograph fitted with a gas density detector. The separation obtained with the investigated column (Arochlor 1232 on Chromosorb T, 40–60 mesh) could be improved by conditioning with water vapour.

REFERENCES

1 D. F. Othmer and R. Nowak, *AIChE J.*, 18 (1972) 217.
2 J. Hille and W. Dürrwächter, *Angew. Chem.*, 72 (1960) 850.
3 H. Runge, *Z, Anal. Chem.*, 189 (1962) 111.
4 R. M. Bethea and M. C. Meador, *J. Chromatogr. Sci.*, 7 (1969) 655.
5 P. K. Basu, C. J. King and S. Lynn, *J. Chromatogr. Sci.*, 10 (1972) 479.
6 F. van de Craats, *Anal. Chim. Acta*, 14 (1956) 136.