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GAS CHROMATOGRAPHIC DETERMINATION OF CARBONATES IN THE CORROSION PRODUCTS OF METALS

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SUMMARY

A method was developed for the gas chromatographic determination of carbonates and oxycarbonates to be used for the analysis of corrosion products formed on the surface of Cu, Zn, Fe, Al and their alloys immersed in sea water.

The samples were treated for 15 min at room temperature with 30% glycine solution, which dissolved the compounds of bivalent metals but left unchanged other corrosion products and the metallic matrix. The carbon dioxide evolved was stripped with a flow of purified inert gas and trapped at liquid nitrogen temperature in the modified loop of a gas sampling valve. It was then thermally desorbed and injected into a gas chromatograph equipped with a Porapak Q column and a thermal conductivity detector.

The sensitivity and linearity of the method were tested in the range 1–5000 ppm of carbon dioxide by using an exponential dilution flask and calibration was effected by dissolving known amounts of carbonates in the stripping unit. The minimum detectable amount was 0.5 μg of carbon dioxide (with an accuracy and precision of about $\pm 5\%$). The method is about 20 times more sensitive than other methods currently used, such as trapping with pyridine and titration with sodium methoxide, or conductimetric measurements. The procedure, with some modifications, can also be used for the determination of carbonates in other types of samples.

The sensitivity limit of the method depends on the area of the corroded specimen, on the trapping efficiency of the sampling loop, on the thermal conductivity detector filament current and, mainly, on the purity of the stripping gas. This is because its impurities are concentrated in the cooled loop and the blank carbon dioxide value is therefore much greater than the actual concentration in the stripping stream.

INTRODUCTION

The corrosion products of metals such as Ni, Cu, Zn and their alloys in sea

water or in brackish water are mainly formed by oxides, oxychlorides, sulphates and basic carbonates[1-4] and may have a thickness varying from a few nanometres (for oxidized nickel specimens)[5] to several millimetres (for zinc)[6]. If the thickness of the corrosion layer is less than 100 nm, qualitative characterization by X-ray diffracto-metric analysis is often imposible, while the Auger technique, which permits the semi-quantitative analysis of thin films ($\leqslant 10$ nm) may sometimes yield inaccurate results owing to the possible transformation of some compounds (e.g., the loss of water of crystallization) or its evaporation in the high vacuum of the instrument (10^{-8} Torr). The interpretation of the Auger spectra is complex, owing to the large number of possible compounds in the corrosion layer whose chemical formula canot be easily deduced from a knowledge of the various elements and their valencies only. The results of instrumental analytical techniques can therefore be improved by classical chemical analysis, in order to obtain the determination of certain ions (e.g., CO_3^{2-}) that cannot be measured by other methods.

The complete qualitative and quantitative identification of the various com-pounds formed by each metal can therefore be carried out by chemical analysis after selective dissolution of the oxidation products with a suitable series of solvents that remove layers of different composition but leave the metallic matrix unchanged, as shown by previous studies[6-8]. A typical series of selective solvents consists of methanol at 65°C, which dissolves chlorides and sulphates, saturated glycine solution at 25°C, which removes compounds of bivalent metals (oxides, carbonates, basic chlorides, sulphates and oxychlorides) and 1% ammonia solution at 25°C, which dissolves other corrosion products excluding monovalent copper sulphide. Cations in the dissolved fractions are determined by atomic absorption spectrometry with flame or electro-thermal atomization and by anodic stripping voltammetry. Some anions (sulphates, chlorides, phosphates) are separated and measured by ion chromatography. Carbon dioxide evolved by the decomposition of carbonates and oxycarbonates during the treatment with glycine solution can be stripped from the reaction vessel by a flow of inert gas and determined by titrimetry[9,10] or conductimetry[11,12].

In the titrimetric methods, the carbon dioxide removed by a stream of nitrogen is absorbed in pyridine or in a mixture of benzylamine, ethanol and dioxane. At the end of the reaction, the absorbed carbon dioxide is titrated with sodium methoxide with thymol blue as indicator. This method permit a minimum detectable amount (MDQ) of about 40 μg of carbon dioxide to be determined when the titrant solution (0.01 M) is added with an automatic microburette that can inject a minimum volume of 10 μl.

Conductometric methods developed for determining small amounts of carbon in steel by measuring the change in conductivity of an alkaline solution where the carbon dioxide stripped by the stream of inert gas is absorbed have sensitivity limits of 2 mg when carbon dioxide-free barium hydroxide[11] and 50 mg when carbon-ate-saturated barium hydroxide solution[12] is used.

These methods may not be sensitive enough for the determination of carbon-ates in the corrosion products of some metals. If the concentration of CO_3^{2-} in the corrosion products is about 5%, as in the corrosion of many metals in sea water, and the thickness of the corrosion layer is about 1 μm (e.g., on copper or zinc surfaces), 10 μg of carbon dioxide may be evolved from 1 cm^2 of apparent surface. By using specimens having a surface area of 20 cm^2, the determination of carbon dioxide is
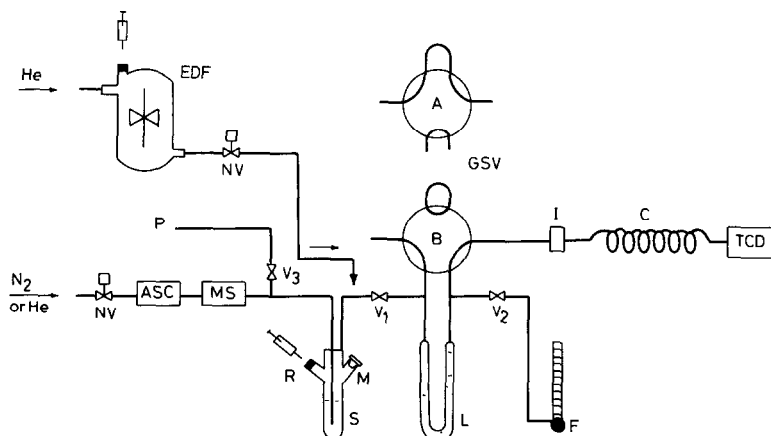
Fig. 1. Schematic diagram of the manifold used for extraction, trapping and analysis of carbon dioxide in corroded specimens. N_2 and He, stripping and carrier gases; NV, needle valve; ASC and MS, ascarite and molecular sieve traps; S, reaction and stripping unit; M, solid sample inlet; R, liquid and gas samples inlet; V_1, V_2 and V_3, on–off valves; L, refrigerated sampling loop; P, vacuum pump; F, bubble flow meter; GSV, gas-sampling valve in fill (A) and analysis (B) positions; I, injection port; C, column; TCD, thermal conductivity detector; EDF, exponential dilution flask for calibration.

possible by both titrimetric and conductimetric methods. On the other hand, the thickness of the corrosion layer formed on the surface of nickel and its alloys ranges between 2 and 30 nm, and in this instance the amount of carbon dioxide evolved from 1 cm^2 of apparent surface may be as low as 0.02–0.3 μg. The sensitivity of the above methods is therefore not high enough for the determination of carbonates in thin corrosion layers. A more sensitive gas chromatographic method was therefore developed that determines the carbon dioxide evolved during the selective dissolution of carbonates and trapped in a suitable manifold.

EXPERIMENTAL

Fig. 1 is a schematic diagram of the system used for the extraction and gas chromatographic (GC) analysis. The carbon dioxide was evolved in the stripper unit by treatment of the corroded specimen (having a surface area of 20 cm^2) at room temperature with 30% glycine solution for 15 min, stripped by a flow of gas purified by ascarite and molecular sieve traps and trapped at liquid nitrogen temperature in the modified loop of the gas sampling valve (GSV) (Varian nut type, six-port, stainless steel). The loop was filled with metallic beads in order to increase the heat exchange and the trapping efficiency. The free volume of the used loop was 2.12 cm^3, measured by interpolation of a series of known-volume injections of nitrogen.

When carbon dioxide had been completely removed from the stripping unit, valves 1 and 2 were closed, sealing the trapped compounds in the loop, which was heated at room temperature in order to vaporize carbon dioxide. By switching the gas sampling valve, the content of the loop was injected into the GC column, filled with Porapak Q, 80–100 mesh (3 m $\times$ 0.32 cm O.D.), thermostated at 55°C and connected with a thermal conductivity detector. A Varian Model 1520 gas chromatograph was used.

RESULTS AND DISCUSSION

The response and linearity of the GC system in the range 1–5000 ppm of carbon dioxide were calibrated by using an exponential dilution flask (EDF) connected to the GSV, where known amounts of carbon dioxide were injected and exponentially diluted by the flow of carrier gas.

As a function of elapsed time t from the injection of carbon dioxide into the EDF, the concentration, C_t, in the GSV is given by

$$\ln C_t = \ln C_0 - \frac{\varphi t}{V_e}$$

where C_0 is the initial concentration, φ is the flow-rate of diluting gas through the EDF, V_e is the effective gas volume in the EDF, *i.e.*, the volume that the amount of gas in the EDF would occupy at normal pressure. The effective volume V_e is needed for two purposes: (1) for the calculation of the initial concentration C_0 in the EDF and (2) for the calculation of the sample concentration at time t, and is calculated by applying Boyle's law, with the hypothesis that, in the pressure range used in practice, the deviations are negligible. The knowledge of the GSV dead volume, of the loop volume and of the loop pressure permitted the absolute amount of carbon dioxide injected to be calculated.

Correlation coefficients ranging between 99.01 and 99.09% were obtained in replicate calibration runs. Each of fifteen injections made during the exponential dilution over a time period of 120 min permitted the carbon dioxide concentration at the outlet of the EDF to decrease from the initial value of 1% to the ppm range.

Some experiments were carried out in order to check the effect of the detector filament current on the sensitivity. By changing the current from 150 to 145 or 155 mA, a change in the peak height of about ±2% was observed and therefore the calibration was found to be effective within this range when the instrument was switched off for an extended period, and the filament current was re-set to the previous value with a ±3% tolerance.

The calibration of the trapping efficiency as a function of the stripping gas flow-rate was carried out by injecting into the manifold, through the inlet M, sealed

TABLE I

TRAPPING EFFICIENCY, MEASURED BY INJECTING KNOWN AMOUNTS OF PURE CARBON DIOXIDE AND EXPRESSED AS A FUNCTION OF THE STRIPPING GAS FLOW-RATE AND OF THE FREEZING TIME

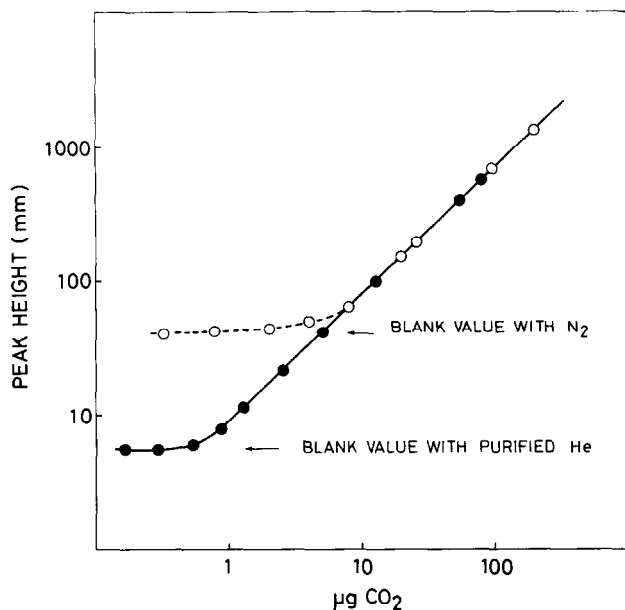| Nitrogen flow-rate (cm³/min)	Trapping time (min)		
	5	12	20
120	—	23	—
55	—	48	—
40	—	61	—
25	45	76	87
15	61	82	95

Fig. 2. Linearity of the determination of carbon dioxide by treating known amounts of sodium carbonate with glycine solution. The MDQ depends on the blank value with nitrogen (○) and purified helium (●) as the stripping gas

by a rubber septum, a constant volume (100 μl) of pure carbon dioxide by means of a gas-tight syringe and measuring the amount recovered after a freezing–heating cycle. Table I shows that satisfactory efficiency is obtained with a low stripping gas flow-rate (15 cm^3/min) and with a freezing time long enough to permit complete washing out of the dead volume of the stripper unit and of the connecting tube. The linearity and reproducibility of the evolution of carbon dioxide from carbonates and of its trapping were tested by treating with glycine known amount of 0.005 M sodium carbonate solution in the stripping unit. With a trapping time of 20 min and a stripping gas flow-rate of 15 cm^3/min a correlation coefficient of 97% was found. An MDQ of about 8 μg of carbon dioxide was achieved with an accuracy and precision of ± 5% when using nitrogen as the stripping gas.

The MDQ of carbon dioxide with the described system depends largely on the purity of the gas used for extraction. Traces of carbon dioxide in the gas are concentrated in the trap by a factor of about 150 (with a flow-rate of 15 cm^3/min and an extraction time of 20 min, the trap volume being about 2 cm^3). Therefore, the purification of the nitrogen stripping gas was critical and was achieved by using ascarite and activated molecular sieve traps. Blank values of about 5 μg of carbon dioxide were obtained, corresponding to an average concentration of 10 ppm of carbon dioxide in the stripping nitrogen (Fig. 2). This blank value was reproducible, can be subtracted from the results of the run and is suitable when the thickness of the corrosion layer is greater than 30 nm or the amount of carbonates is greater than 5%.

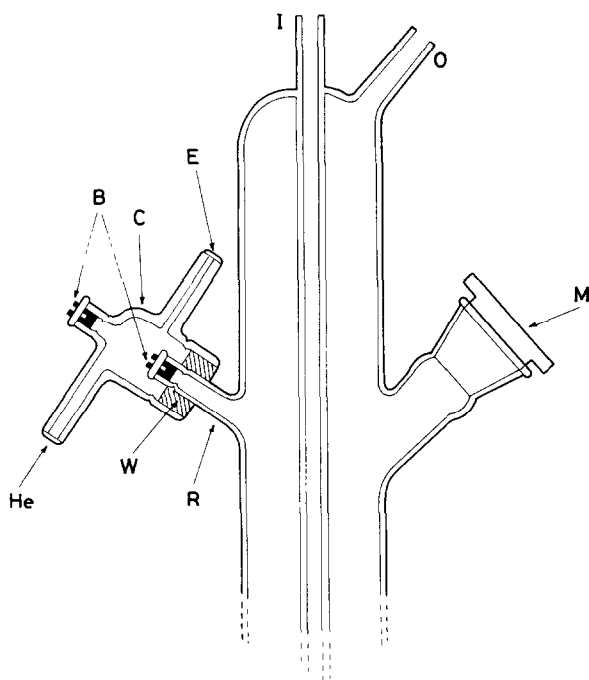A further improvement in the sensitivity of the method is achieved by using

Fig. 3. Detailed drawing of the upper part of the stripping unit, with purge chamber for decreasing the sample contamination by air and carbon dioxide. I, stripping gas inlet; O, gas outlet; M, solid sample inlet; R, gas and liquid samples and reactives inlet; W, rubber washer; C, purge chamber; B, burrel septa; E, capillary exit; He, purified helium inlet.

as the stripping gas helium highly purified by cooling the molecular sieve trap in liquid nitrogen. In this instance, rubber and plastic tubings are avoided in the stripping circuit and an all-metal–glass system must be used. The injection of the liquid calibration samples and of reactants in the extraction tube is made through a double burrel septum, with purified helium flowing in the purge chamber, in order to remove any carbon dioxide diffusing through the rubber septum exposed to the atmosphere (Fig. 3). Blank values 10–20 times smaller than these obtained with nitrogen were found with this technique (Fig. 2) and therefore the MDQ of the method is substantially smaller, being about 0.5 μg of carbon dioxide, mainly when the system is carefully flushed with purified helium after the introduction of the corroded specimen into the reactor S through the inlet M. By connecting the system to a vacuum pump, P, through valve V_3, the degassing of the sample is accelerated. Vacuum is also used during the regeneration of the molecular sieve absorbing trap. Carbon dioxide-free glycine solution, obtained by bubbling purified helium in its bottle and by taking the necessary amount of liquid through a perforable septum by means of gas-tight syringe, is also used in order to reduce the blank values, leading to a further decrease in the MDQ, down to the sensitivity limit of the GC detector, and to an ultimate sensitivity much greater than that obtained with conductimetric and titrimetric methods.

Determinations of carbonates in the corrosion layer of differents metals were

TABLE II

CONCENTRATION OF CARBONATES IN THE CORROSION PRODUCTS OF VARIOUS METALS, AND PRECISION OF THE DETERMINATION (AVERAGE FOR THREE CORRODED SPECIMENS)

Sample	Exposure time to sea water (h)	CO_3^{2-} ($\mu g/cm^2$)
Cu–Ni alloy (70:30)	120	13.30 ± 0.05
Ni	360	0.89 ± 0.07
Cu	330	55 ± 5
Zn	350	148 ± 10

carried out with the GC technique, and the results given in Table II (averages for three samples) were obtained. The precision of these values is satisfactory, taking into account the possible difference in the corrosion products from different specimens, variations in the corrosive solutions, temperature, etc.

The absolute accuracy of a method such as this is difficult to evaluate when thin corrosion layers are analysed, because no comparison with other techniques is possible and standards of known composition are not available.

X-ray diffraction analysis of specimens after the glycine treatment, however, showed that carbonates previously detected were completely removed, and therefore the carbon dioxide trapping efficiency and the accuracy of the method achieved in the analysis of sodium carbonate standards will probably also be obtained in the analysis of real samples.

ACKNOWLEDGEMENT

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