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A NEW TECHNIQUE FOR ANALYSIS OF EVOLVED GASES FROM A THERMOGRAVIMETRIC ANALYZER *

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ABSTRACT

Thermogravimetry is a powerful technique for materials characterization. It provides valuable information on mass changes of the sample under controlled heating conditions. The extent and kinetics of reactions involved can also be determined. However, it relies on a combination of other analytical techniques to identify the nature or determine the composition of the evolved gases or the remaining residue. This paper describes a new technique for rapid and convenient detection and determination of selected components in evolved gases from a thermogravimetric analyzer without any modification of the analyzer. Disposable devices are used to collect the sample gases, store the necessary reagents, perform the chemical reactions, and produce the final analytical results. The features and applications of the technique are illustrated with pertinent examples.

INTRODUCTION

Thermogravimetry is a powerful technique widely used for materials characterization. It provides valuable information on weight changes of the sample under controlled heating conditions. Thus, the extent and the kinetics of the reaction under investigation can be readily obtained. However, this technique relies on a combination of other analytical techniques to determine the nature and composition of the evolved gases from the thermogravimetric analyzer. Commonly used techniques for this purpose include gas chromatography, infrared spectroscopy, mass spectrometry, and titrimetry [1]. This paper describes a new approach to rapid analysis of evolved

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gases from a thermogravimetric analyzer without any modification of the analyzer.

The new technique, packaged evolved gas analysis (PEGA), is defined as a technique for rapid and convenient detection and determination of selected components in evolved (but not necessarily thermally) gases using disposable devices which collect the sample gases and/or store the required reagents, and perform chemical reactions to produce the final analytical results. The technique features inexpensive equipment, disposable sampling/analysis devices, minimum technical skills of the user, fast analysis, easy adaptation to the sample source, high sensitivity, good precision and accuracy, and either qualitative or quantitative analysis.

EXPERIMENTAL

The DuPont Model 951 thermogravimetric analyzer controlled by a DuPont 1090 programmer/plotter was used for this work. The connecting system interfacing the thermogravimetric analyzer and the collecting device is shown in Fig. 1. Two types of disposable collecting/analysis devices are devised. The first type employs a disposable analysis pack made of an optically clear inert polymeric film material as shown in Fig. 2. The pack contains one large chamber for storing the absorbing solution, and a series of small blisters for storing reagent solutions. This configuration is very similar to the DuPont PRO – TEK colorimetric air monitoring badge system but without the multicavity gas diffuser [2]. The reagent solutions can be forced into the absorbing chamber through the break-seal by pressing on the reagent blisters. Thus, a pre-designed reaction occurs to produce a color or other property change which can be measured to provide the analytical results. For a color reaction, the intensity of the color is conveniently

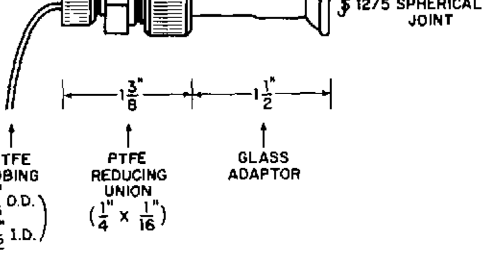

Fig. 1. Interface.

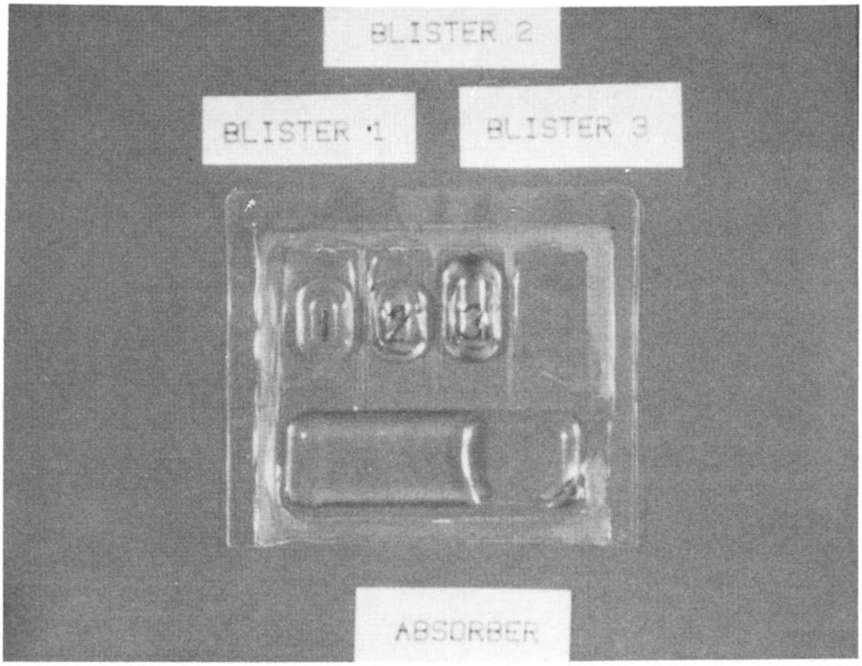

Fig. 2. Disposable plastic analysis packs.

measured with a DuPont PT-3 readout unit [2]. This simple spectrophotometer is calibrated with a calibration card specific to a certain wavelength.

The second type of disposable analysis system (Fig. 3) consists of reagent cartridges made of shrinkable fluorocarbon polymer tubing the dimensions of which are approximately 8 mm OD × 50–80 mm length with a wall thickness of ca. 0.3 mm. These cartridges for storing both collecting solution and reagent solutions are chemically inert, easily heat-sealed, easily cut-opened when ready to use, and disposed of after analysis. One additional feature of this type of tubing is the complete draining of the liquid thus securing volume accuracy. Currently, these cartridges are used in conjunction with disposable polystyrene or acrylic cuvettes for spectrophotometric measurements in any suitable commercial spectrophotometer such as a Spectronic 100 by Bausch and Lomb.

The analysis procedure is quite simple. The thermogravimetric measurement is carried out in a standard manner with a gas flow rate at 30–100 ml min^{-1} depending on the rate of absorbing reaction. A proper choice of sample weight is desirable to suit the sensitivity of the measuring device. If necessary, microgram quantities of a sample can be introduced to the analyzer in solution form, and then the solvent removed by evaporation as guided by the weight loss curve. The capillary of the interface is inserted into the absorbing solution through a punched hole either in the plastic pack or

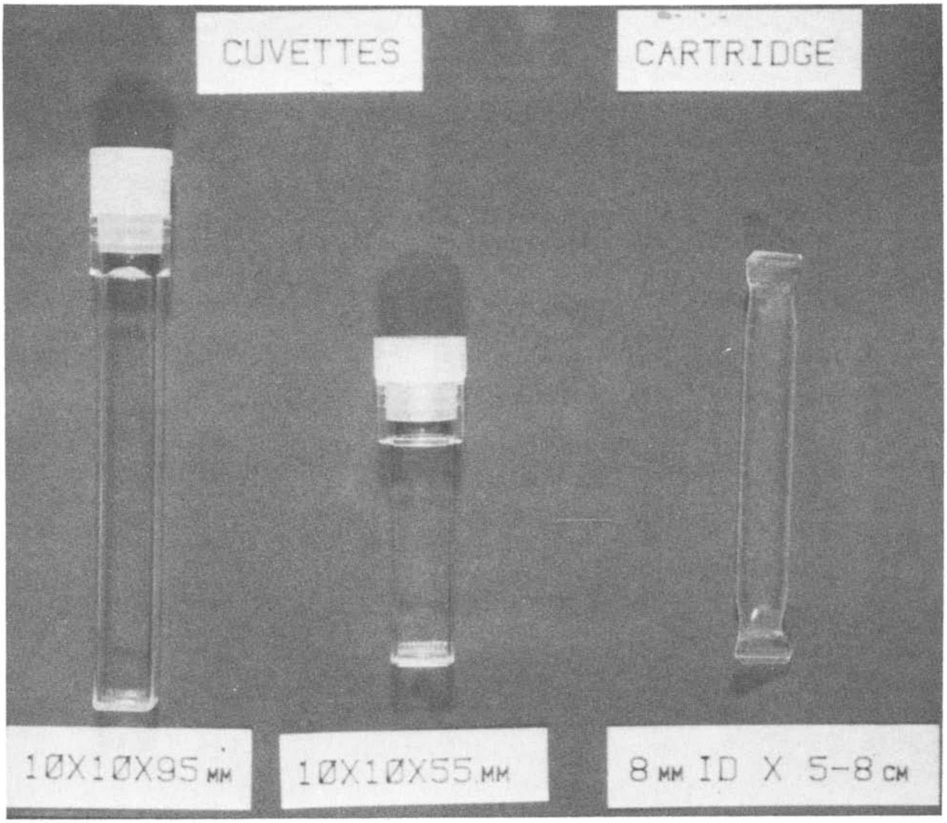

Fig. 3. Disposable analysis system consisting of reagent cartridges and cuvettes.

in the capped cuvette. After gas collection, the reagents are added and the subsequent spectrophotometric measurement is routine.

RESULTS AND DISCUSSION

Determination of sulfur

The sulfur content of a sample is frequently determined by oxidizing it to sulfur dioxide. An evolved gas analysis technique for sulfur dioxide thus provides a convenient method for compositional analysis of sulfur-containing substances. A sensitive colorimetric method has been successfully applied for determination of sulfur dioxide in air [2,3]. In the present work the following recipe is used:

Collecting solution. Potassium tetrachloromercurate (2 ml 0.004 M).

Reagent blisters. (1) 0.35 ml 0.06 M sulfamic acid; (2) 0.35 ml 0.04 M

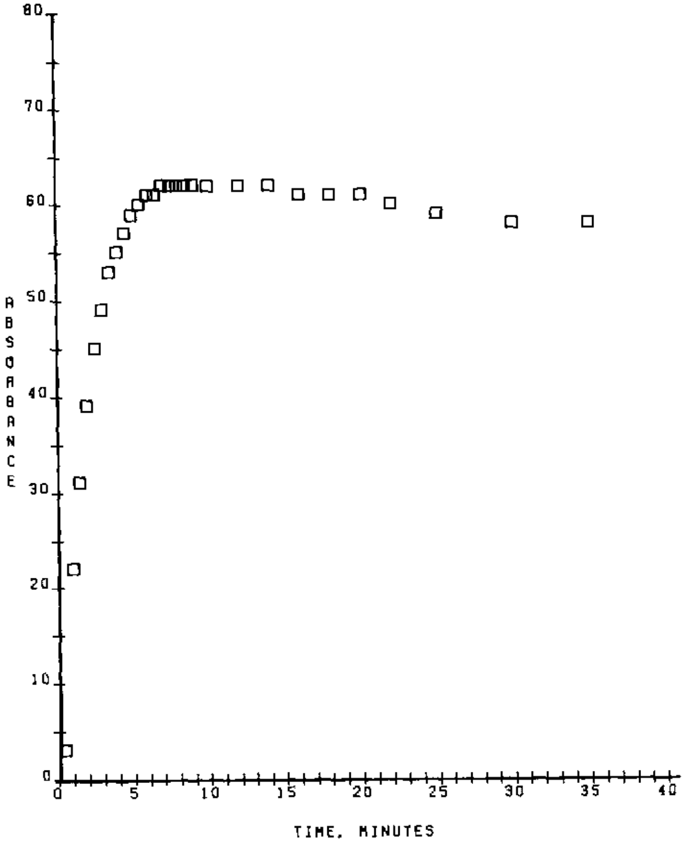

Fig. 4. Time dependence of absorbance for SO_2 determination. (□) 40 μl sulfite solution (8.1 μg SO_2).

formaldehyde; (3) 0.5 ml 5×10^{-4} M pararosaniline hydrochloride in 2.4 M phosphoric acid.

Reactions. $(HgCl_4)^{2-} + SO_2 \rightarrow [Hg(SO_3)_2]^{2-}$; $Cl\text{-}C\text{-}(C_6H_4NH_3^+)_3$ + HCHO + $[Hg(SO_3)_2]^{2-} \rightarrow$ alkyl sulfonic acid chromophore (red violet, 560 nm).

Blister 1 is not used unless there are nitrogen oxides present which can interfere with the analysis. The reaction reaches equilibrium in about 7 min under the present conditions as shown in Fig. 4. All the aqueous solutions should be prepared with freshly distilled or carefully deionized water and checked for blank values by the spectrophotometer.

The calibration curve is constructed with known amounts of aqueous sodium sulfite solution (typically 0.2 μg μl^{-1}). The actual concentration of the sulfite solution is determined by the iodine method [3]. A typical calibration curve is shown in Fig. 5. The calibration points are obtained by adding various amounts of the sulfite solution into the absorbing solution chamber of the plastic pack, and performing regular thermogravimetric runs

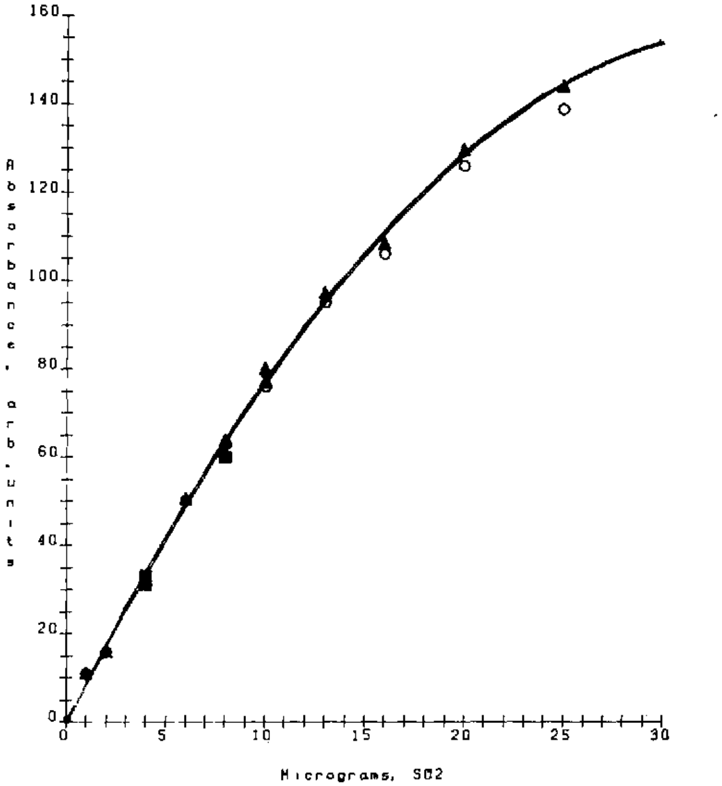

Fig. 5. Calibration curve for SO_2 determinations. (▲) He flow 30 ml min^{-1}; plastic packs; dilution corrected. (○) As above, before dilution correction. (———) $-0.129965x^2 + 9.047642x - 0.488065$. (■) Sodium dithionate data, same conditions.

with helium gas flowing through the absorbing solution. The reduction of the absorbance due to the additional volume of the sulfite solution should be corrected as shown in Fig. 5. The calibration curve appears to obey Beer's Law up to ca. 15 μg of sulfur dioxide as shown in Fig. 6.

In order to check the accuracy of the method, we have investigated a wide variety of organic and inorganic materials and found sodium dithionate dihydrate to be a good reference material. As shown in Fig. 7, this material loses 14.7% by weight at 50–110°C and 26.5% at 250–300°C, which correspond to 2 moles of water and 1 mole of sulfur dioxide per 1 mole of sodium dithionate dihydrate precisely. This is in agreement with a previous study by House et al. [4]. We have also confirmed water and sulfur dioxide as the only gases evolved during these two weight loss steps by a coupled thermogravimetry–mass spectrometry technique [5]. Data for samples of sodium dithionate dihydrate analyzed by the present disposable analysis pack method are shown in Figs. 5 and 6. The agreement is excellent. For all practical purposes, therefore, this reference material can be used for calibration. A

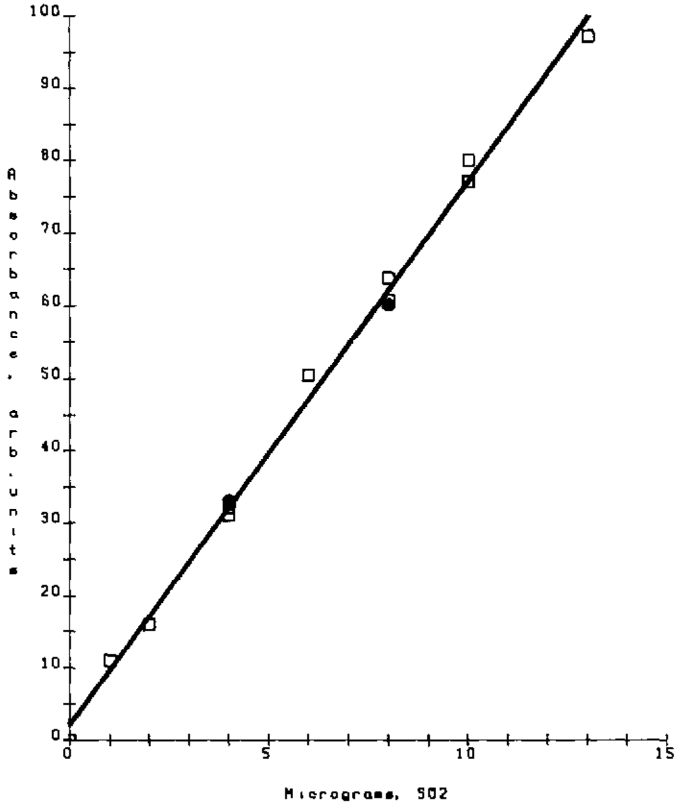

Fig. 6. Linear calibration curve for SO_2 determinations. (□) He flow, 30 ml min^{-1}; plastic packs; dilution corrected. (———) 7.527882x +2.010772. (●) Sodium dithionate data, same conditions.

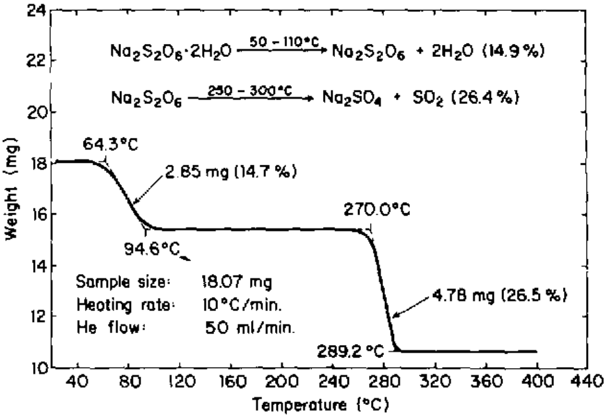

Fig. 7. TG of sodium dithionate dihydrate.

concentration of 75.5 mg sodium dithionate dihydrate in 100 ml aqueous solution provides a solution containing 0.2 μg of sulfur dioxide per μl.

Determination of chlorine

A method has been developed for determination of hydrogen chloride in evolved gases. This example is used to demonstrate the disposable cartridge and cuvette technique. The evolved HCl is absorbed in a disposable cuvette with aqueous sodium acetate as the absorbant [6] added from a cartridge. Other reagents and possible reactions are shown as follows [7]:

Collection solution. Aqueous sodium acetate (2 ml 0.5 M).

Reagent blisters. (1) 0.5 ml 0.13 M ferric ammonium sulfate in 6N HNO_3; (2) 0.25 ml 0.01 M mercuric thiocyanate in methanol.

Reactions. $2Cl^- + Hg(SCN)_2 \rightarrow HgCl_2 + 2CNS^-$; $4Cl^- + Hg(SCN)_2 \rightarrow HgCl_4^{2-} + 2CNS^-$; $CNS^- + Fe^{3+} \rightarrow Fe(CNS)^{2+}$ (red, 470 nm).

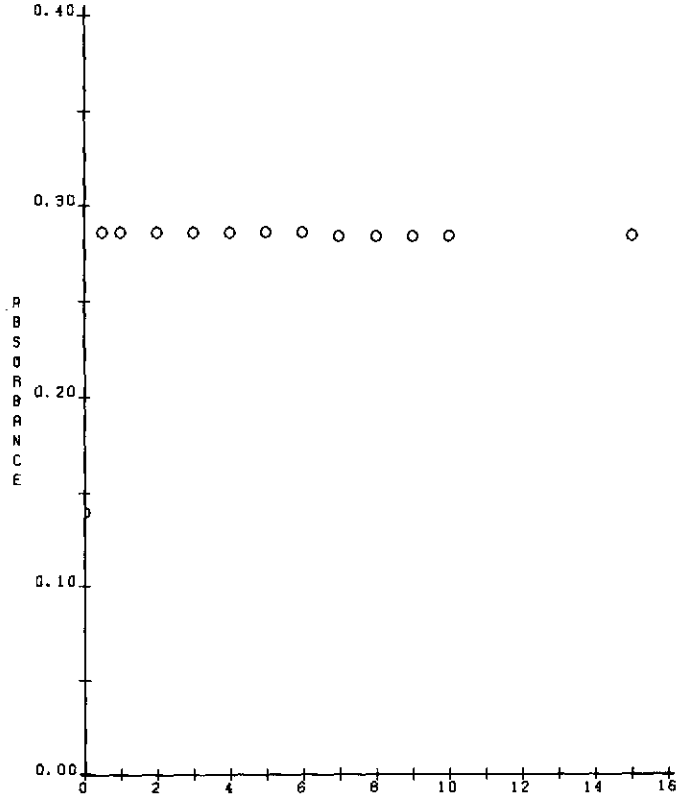

Fig. 8. Time dependence of absorbance for chloride determinations. (○) 50 μl NaCl solution (10 μg Cl).

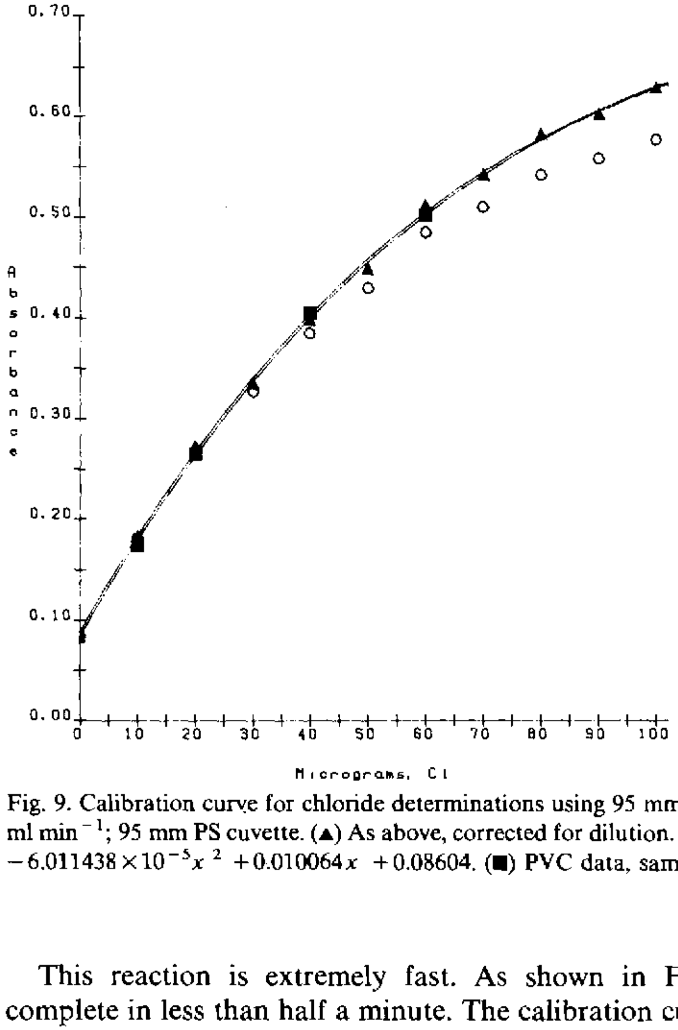

Fig. 9. Calibration curve for chloride determinations using 95 mm cuvettes. (○) He flow, 100 ml min^{-1}; 95 mm PS cuvette. (▲) As above, corrected for dilution. (———) $1.374002\times10^{-7}x^3 - 6.011438\times10^{-5}x^2 + 0.010064x + 0.08604$. (■) PVC data, same conditions.

This reaction is extremely fast. As shown in Fig. 8, the reaction is complete in less than half a minute. The calibration curve for this analysis is constructed with known amounts of aqueous sodium chloride (0.2 μg Cl/μl) and shown in Fig. 9. It should be noted that the curve does not go through the origin because of the trace amount of chloride present in the water. The level of this blank depends on the vigor of purification of the water used for preparing the reagents, and should also be measured. Again, the calibration curve is linear up to ca. 20 μg. However, for practical use, a calibration curve over a wide range is preferred. As in the case of sulfur dioxide, the volume of the sodium chloride solution should be corrected for the absorbance readings.

Considerable effort has been made to find a good reference material for chloride analysis. Finally, we found additive-free polyvinyl chloride to be a good choice. This polymer degrades to release hydrogen chloride quantitatively [1,8]. A proper weight of the sample can be placed in the thermobalance by using its solution in cyclohexanone. A typical thermogravimetric

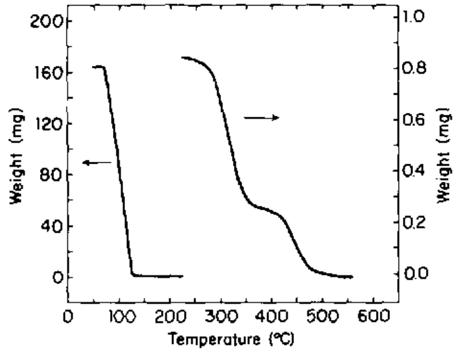

Fig. 10. TG of PVC in cyclohexanone solution, 43.50 mg/100 ml. Sample size: 164.48 mg; heating rate: 10°C min^{-1}; He flow: 100 ml min^{-1}.

curve of its solution is shown in Fig. 10. The solvent is removed at ca. 200°C before a stepwise decomposition occurs. Hydrogen chloride is produced mainly during the first weight loss step, but the amount cannot be measured from the weight loss because of the presence of other products. However, collection of the evolved gases through the complete reaction does not affect the analysis. Some polyvinyl chloride data are shown on the calibration curve in Fig. 9. The agreement is excellent. The precision of the measurement is typically 1% as shown in Table 1 for 7 separate runs. Once a reference material has been established, it can be used to calibrate new preparations of reagents and to confirm new procedures. For instance, the previous calibration curve is constructed using 95 mm polystyrene cuvettes. A new calibration curve is now constructed with 55 mm acrylic cuvettes as shown in Fig. 11. Even though the curve is different from before, the polyvinyl chloride points still fall on the curve as long as they are obtained under identical conditions.

TABLE 1

Precision study: determination of Cl in PVC

Volume of solution (μl)	Cl calculated (μg)	Absorbance	Cl by PEGA (μg)
50	10	0.278	10.0
50	10	0.281	10.2
50	10	0.275	10.0
50	10	0.273	9.9
50	10	0.281	10.2
50	10	0.282	10.2
50	10	0.275	10.0
			Mean: 10.1
			Std. Dev: 0.13

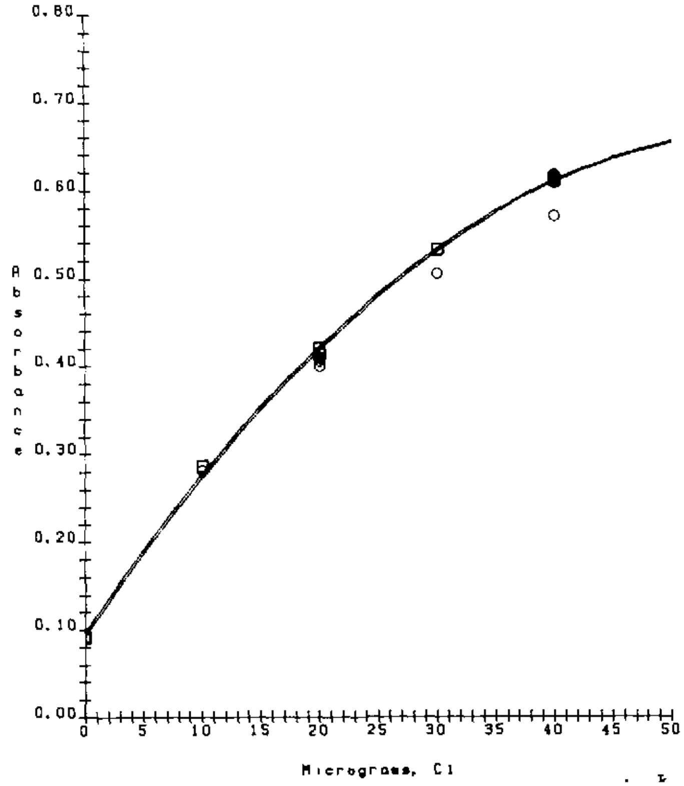

Fig. 11. Calibration curve for chloride determination using 55 mm cuvettes. (○) He flow, 100 ml min^{-1}; 55 mm acrylic cuvette. (□) As above, corrected for dilution. (———) $-1.700944 \times 10^{-4}x^{2} + 0.019655x + 0.094973$. (●) PVC data, same conditions.

Composition and stability of chlorosulfonated polyethylene

Chlorosulfonated polyethylene (CSPE) elastomer contains ca. 1–1.5% sulfur and 25–40% chlorine the determination of which requires a tedious procedure typically involving a Schöniger oxygen combustion followed by electrochemical analysis. We have determined the decomposition behavior of a typical commercial sample of CSPE using combined thermogravimetry–mass spectrometry [5]. As shown in Fig. 12, sulfur dioxide, as represented by m/e 64, is produced during the first weight loss step of 2.7%, while HCl, represented by m/e 36, is released during the second weight loss step of ca. 40%. When the evolved sulfur dioxide is analyzed using the disposable plastic pack method and the calibration curve in Fig. 5, the %S values are shown in Table 2, which are in good agreement with those obtained by Schöniger oxygen flask combustion followed by potentiometric titration with lead perchlorate. The amount of Cl in the polymer is determined using the disposable cartridge-cuvette system and the calibration

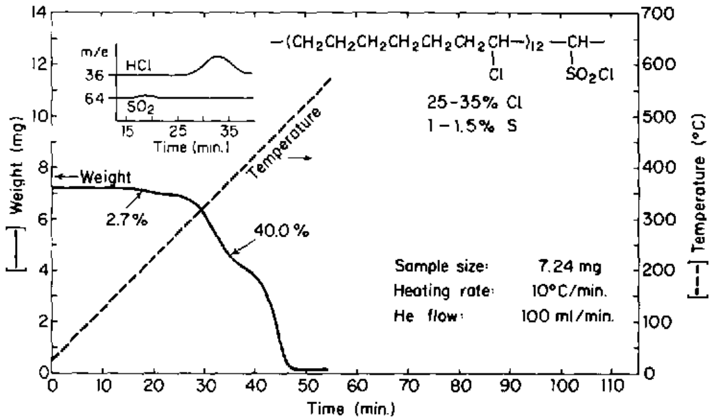

Fig. 12. TG–MS of CSPE.

curve shown in Fig. 9. The results are shown in Table 3, and in good agreement with those obtained by Schöniger oxygen flask combustion followed by coulometric generation of silver ions with amperometric detection of the end point. For the above determinations, the CSPE sample is introduced into the thermobalance in cyclohexanone solution.

The advantages of using the thermogravimetric analyzer to produce the gaseous products are its capability to control the heating conditions and the valuable weight loss information. The value of weight loss information is evident in the case of sodium dithionate dihydrate. The feature of heat control is best illustrated by the study of the stability of CSPE. This information is desirable in proper processing and use of the elastomer. As shown in Table 4, the stability of CSPE has been determined at 150°C for 1 h and at 100°C for 1 h. Both sulfur dioxide and HCl produced are measured. The precision is better than 5%.

TABLE 2

Determination of %S in CSPE

%S by PEGA	%S by combustion
1.10	1.08
1.03	1.09
1.11	1.08
1.08	1.01
1.08	1.03
1.05	1.03
1.01	
1.05	
Mean: 1.06	1.05
Std. Dev: 0.04	0.03

TABLE 3

Determination of %Cl in CSPE

% Cl by PEGA	%Cl by coulometry
34.0	34.7
35.0	35.3
34.8	34.5
36.4	
35.0	
Mean: 35.0	34.8
Std. Dev: 0.77	0.34

TABLE 4

Stability of CSPE

Conditions	SO_2 released	%HCl released
1 h/150°C	1.06	0.077
	1.18	0.081
	1.12	0.085
	1.06	0.081
	Mean: 1.11	0.081
	Std. Dev: 0.06	0.003
1 h/100°C	0.01	
	0.01	
	0.01	
	0.01	
	0.01	
	Mean: 0.01	
	Std. Dev: 0.00	

CONCLUSION

A packaged evolved gas analysis system has been described, and illustrated with some practical examples. Both precision and accuracy are considered to be excellent. This new approach of evolved gas analysis is expected to be generally applicable to study of stability and degradation, determination of residual solvent, monomer and additives, evaluation of contamination, compositional analysis, quality control, investigation of kinetics and mechanism, studies on toxicity, and process control.

ACKNOWLEDGMENT

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