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DETERMINATION OF CARBONATES IN DETERGENTS BY GAS CHROMATOGRAPHY

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SUMMARY

Head-space analysis was applied for the determination of carbonates in detergents, based on their decomposition by mineral acid solution, followed by equilibration and gas chromatographic analysis of the gas phase for CO₂ determination on a Porapak column using thermal conductivity detection. Water traces are retained by the silica gel layer in the injection port. The calibration is performed using a Na₂CO₃ standard. Chromatograms are evaluated measuring CO₂ peak heights. Collaborative testing in seven laboratories showed a repeatability up to 2% from the result in one laboratory and a reproducibility of 3–6% from the inter-laboratory results. The method was applied for analysis of commercial detergents with good results.

INTRODUCTION

Standard methods for carbonates determination in detergents are based on the decomposition of the carbonates in acid solution^{1–4}; the CO₂ liberated is either absorbed in NaOH or a solution of the latter and determined by titration or weighing, or is measured from the mass loss of the original samples. In all procedures, special all-glass devices are necessary. Another, simple procedure, combining titration steps with two indicators under CO₂ elimination⁵ suffers from interference from phosphates and peroxoborates. Other decomposition/titration methods^{6,7} do not show any better performance. An instrument has been described⁸ for detergent sample decomposition by mineral acid, where the total gas phase was separated for CO₂ determination by gas chromatography (GC). Another variant has been developed for carbonates determination by reaction GC based on CO₂ determination, where the sample solution is injected into a pre-column reactor, packed with supported H₂SO₄⁹.

My idea was to apply head-space GC analysis¹⁰ for carbonates in detergents after CO₂ liberation in a closed vessel and equilibration. A simple procedure was developed and successfully tested¹¹: it appeared to be more reliable and rapid than previous methods. In the meantime, a similar method was applied for the determination of free and bound CO₂ in the sea-water¹². The aim of this note is to provide information on the principle and practice of the new method and present some data on the testing of its reproducibility.

METHODS

A detergent sample is weighed and dissolved in water in a volumetric flask. An aliquot volume, *e.g.*, 20 ml from 100 ml, containing about 100 mg Na_2CO_3 , is pipetted into an appropriate glass or polyethylene flat bottomed cylindrical vessel, *e.g.*, a weighing bottle, which is placed upright on the bottom of a wide-necked reaction flask of suitable volume (500 ml) having a septum screw-closure. On the flask bottom, 110 ml of an acid solution are added, *e.g.*, 20 ml of 2 M H_2SO_4 and 90 ml water. Then the flask is closed and the contents shaken well, so that the detergent solution is mixed with the acid solution. The time necessary for equilibrating the liberated CO_2 concentrations in both the liquid and vapour phases is about 1 h. For GC analysis, the sampling of vapours is performed through the septum by use of a syringe of 1- or 2-ml volume. The analyses are performed on a column packing enabling sufficient separation of CO_2 from other air constituents, N_2 , O_2 , etc. The moisture in the gas sample is retained by the silica gel layer in the injection chamber. A thermal conductivity detector is used, with H_2 or He as carrier gas.

For evaluation of the results, a calibration is necessary using standard Na_2CO_3 solution (10 mg ml^{-1}), which is handled similarly to the detergent sample solution. Aliquots of standard solution, corresponding to amounts of Na_2CO_3 lower and higher than the determined content in the sample aliquot analyzed, *e.g.*, 80 mg and 120 mg Na_2CO_3 for 100 mg Na_2CO_3 in the sample, are pipetted into the bottles placed in reaction flasks. To the flask bottom are added 20 ml of 2 M H_2SO_4 , sample matrix and water so as to adjust the total liquid volume to 130 ml. The sample matrix is prepared either by titration of a corresponding aliquot of the detergent sample solution, *i.e.*, 20 ml, by HCl using methyl orange as indicator followed by heating to remove CO_2 , or by ion exchange of this aliquot on strong cation-exchange resin, *e.g.*, Dowex 50W-X8 [H^+] in a short column, where carbonates are retained and decomposed completely.

The mean peak height of CO_2 is calculated from five successive analyses for each sample and both calibration standards, assuming a constant volume of gas sample from the reaction flasks. From these values for both standards and sample, the results can be expressed either in terms of mg Na_2CO_3 in the sample aliquot or of % Na_2CO_3 in the original detergent sample.

Instruments

For GC analyses, a Chrom 5 instrument (Laboratory Instruments, Prague) was fitted with a thermal conductivity detector. A stainless-steel column (120 cm \times 4 mm I.D.) was packed with Porapak Q (80–100 mesh) and operated at 50 or 60°C. The injector was operated at 30–60°C and the detector at 100°C. The carrier gas (hydrogen) flow-rate was 25–30 ml min^{-1} . These operating conditions enabled sufficient separation of CO_2 as a sharp peak of satisfactory symmetry. For gas sampling and injection, glass syringes of 1- or 2-ml volume were used or a bypass sampling loop designed in this laboratory.

DISCUSSION

In the method development, optimum results were achieved with detergent

sample aliquots containing 50–200 mg Na_2CO_3 and a reaction flask volume of 500 ml, including 130 ml total liquid phase and the remainder as gas phase. The results were not influenced by the selection of sample and the method of treatment with acid solution: *e.g.*, direct weighing of the sample into the cylindrical vessel is possible, then mixing the dry original sample with 130 ml of acid solution, etc. The time necessary for equilibration of the distribution of CO_2 between the liquid and gas phases was found to be 1 h. Using shorter times, a broader dispersion of results occurred; longer equilibration times give no substantial change in results.

Using syringes for sampling and injection, in some cases errors were caused by loss of CO_2 . It seems, that practice is necessary until the maximum repeatability of peak heights is achieved. More reliable results were achieved using the bypass sampling loop. By numerous blank tests of air samples, it was shown that, under these operating conditions, correction for trace CO_2 from the air in gas phase samples was not necessary. The elimination of the water component from gas phase samples by its simple retention on the silica gel layer in the injection chamber was highly efficient. Many GC analyses can be performed before an exchange of the silica gel is necessary. For equilibration, it is important to maintain the same environmental temperature for both sample and standards (at ambient temperature).

It is very important to perform a calibration by use of standards for each sample or group of samples, because the peak height as a quantitative parameter is very sensitive to small changes in operating conditions. Under the given operating conditions, about 90 sec were necessary for each GC analysis; for the complete GC analysis including five replicate determination for sample and both standards, 25–30 min are necessary. Even when taking the account of the equilibration time, more than 20 samples can be analyzed in 8 h by one operator on one GC instrument. Good repeatability was found, in the range 1.2–2.5% for the CO_2 peak height.

The repeatability and reproducibility of the final results was checked by collaborative analysis in seven laboratories of standard solutions and of various detergent samples. The procedure was strictly standardized, whereas the GC operating conditions were only as recommended, because different GC instruments were available in the separate laboratories. Five replicate GC analyses were performed for each sample or standard and two final results were required for each sample tested. The statistical treatment of results was performed according to a standard procedure for collaborative analyses¹³. Results from the collaborative testing of three samples are summarized in Table I and demonstrate the reliability of the method. The repeatability (within laboratories) was better than usually achieved in GC analyses and the reproducibility (between laboratories) was similar to that of other GC methods. The mean results from all seven laboratories are in excellent agreement with the known true Na_2CO_3 content in the samples. Standard deviations are lower than 2%; mean standard deviations in the individual laboratories were 0.14–0.44, indicating that all participants had performed their analyses with appropriate care.

In Table II some results are shown for parallel determinations of Na_2CO_3 by GC in various detergent products. These results were in agreement with the known carbonates content, whereas using a previous standard procedure⁴ lower contents were found (up to 2% less).

TABLE I
RESULTS FROM COLLABORATIVE TESTING

	% Na ₂ CO ₃ in samples		
	A	B	C
Mean results, \bar{x}	9.93	20.08	30.01
True (known) result, μ	10.00	20.00	30.00
Absolute error as difference, $\Delta = \mu - \bar{x} $	0.07	0.08	0.01
Standard deviation, s	0.17	0.33	0.23
Repeatability, r	0.22	0.02*	0.48
Reproducibility, R	0.57	0.62*	0.96
	As % of results		
	A	B	C
Absolute error, Δ	0.7	0.4	0.03
Standard deviation, s	1.70	1.65	0.77
Repeatability, r	2.2	0.1	1.6
Reproducibility, R	5.7	3.1	3.2

* After elimination of outliers by testing.

TABLE II
CARBONATES DETERMINATION IN VARIOUS DETERGENTS

Results are given as % Na₂CO₃. x_1 and x_2 are first and second results, respectively, and \bar{x} is the mean of both.

	x_1	x_2	\bar{x}
Wetting detergent	29.3	29.3	29.3
Alkali detergent	32.7	32.1	32.4
Detergent for public laundries	23.1	23.0	23.05
Detergent for textile industry	19.6	20.1	19.85
Universal washing powder	18.1	18.0	18.05
Enzymatic detergent	13.0	13.5	13.25
Washing powder with peroxoborate	10.3	10.9	10.6

CONCLUSIONS

The new procedure for carbonates determination in detergents is more reliable than other methods¹⁻⁹. It can be applied to any commercial detergent or other product containing carbonates. Owing to its selectivity, any interference from other volatile or gaseous components is excluded, e.g., O₂ liberated from peroxo salts, moisture, SO₂ and perfumes. The presence of phosphates, surfactants, alkali and other components in detergent formulations does not influence the results. No special instrumentation is needed. The up to 2% repeatability and up to 6% reproducibility are fully satisfactory for routine operations; series of 20 samples can be analyzed during 8 h.

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