Journal of Chromatography, 108 (1975) 365–369
© Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 8212

Note

Continuous trinitrotoluene process studies

V. Liquid chromatographic analysis of nitration acids

C. D. CHANDLER and W. T. BOLLETER
Hercules Inc., Radford Army Ammunition Plant, Radford, Va. 24141 (U.S.A.)
(Received January 28th, 1975)

One of the most important factors in obtaining good nitration in the continuous trinitrotoluene process[1,2] is control of the nitric acid concentration in each of the nitration vessels. Since the total acidity, expressed as per cent sulfuric acid, varies from 72% in toluene mononitration to 108% (oleum) in trinitration, analysis of nitric acid in this acidity range represents a formidable problem. The nitrating acids also contain various amounts of entrained and soluble nitrotoluenes which pose an additional problem with sample consistency.

Previously the determination of nitric acid concentration in each vessel required diluting a known volume of acid with a known volume of water and titrating an aliquot of the diluted sample with standard ferrous ammonium sulfate to a "dead stop" amperometer end point[3]. The nitric acid concentration was calculated by assuming a standard sample weight and a constant amount of soluble nitrotoluenes in each acid sample. During periods of unstable operation, the amount of nitrotoluenes in the acid phase increased, producing apparent low results for the nitric acid concentration. Nitric acid flow was then increased to the vessel in question to correct the apparent, but erroneous, deficiency, thus compounding the problem.

A method was developed to correct for the nitrotoluene content wherein a sample of the acid phase to be analyzed was added to a calibrated test tube and allowed to stand in a steam-bath for approximately 10 min. During this time entrained nitrotoluenes separated, permitting a measure of the true volume of acid taken for analysis. This correction technique did improve control of the nitration process but was time consuming; therefore, a new analytical approach free from such limitations was needed to provide more stable operation of the nitration process. An additional objective was to develop a method that would also be amenable to on-line sampling and analysis.

Various techniques have been used for the determination of nitric acid. In addition to the titration method mentioned above, nitric acid can be determined in the presence of sulfuric acid by the nitrometer[4] method or UV absorption at 301 nm[5]. However, the nitrometer method is too time consuming and the UV method suffers from interference by dissolved nitrotoluenes.

Nitric acid has been determined in oleum mixtures with a nitrate-specific ion electrode but requires accurate dilutions with water because of the extreme sensitivity of the electrode to nitrate ions[6].

Determination of nitrate by strong anion-exchange chromatography has also been demonstrated[7]. The ion-exchange approach requires precise preparation of buffers for use as the mobile phase, which poses a problem for on-line analysis. Neddermeyer and Rogers[8] have demonstrated separation of various inorganic sulfate and nitrate salts by gel filtration liquid chromatography (LC). This technique appeared to satisfy our requirements and therefore was investigated for the separation of sulfuric and nitric acids.

EXPERIMENTAL

Apparatus

The LC separations were performed on a laboratory-constructed chromatograph consisting of a Milton Roy Instrument (Model 196-57) minipump and a Laboratory Data Control conductivity detector. The analytical column was 1-m × 3/8-in.-O.D. stainless steel packed with Sephadex G-10 (Pharmacia, Piscataway, N.J., U.S.A.) polydextran resin. The column end fittings contained stainless-steel frits with 50 μ on the inlet and 10 μ on the exit.

The column was slurry packed after swelling the resin overnight in methanol. Solutions with progressive amounts of water were then pumped through the column to obtain maximum swelling. The column was conditioned by pumping 500 ml of 0.2 *M* aqueous sodium hydroxide solution followed by 500 ml of distilled water.

A 25-μl Disc Instrument sampling valve was used to introduce the sample onto the chromatographic column. A Hewlett-Packard (Model 3370A) integrator was used for determination of peak areas.

Sample preparation and analysis

Approximately 5 ml of the nitration acid was carefully diluted with a threefold excess of water in a 25-ml serum bottle to promote separation of the organic and aqueous phases. The sample is diluted to precipitate the nitrotoluenes and to prevent nitration of the polydextran resin. An aliquot of the aqueous phase was then loaded into the sample valve loop via syringe. Elution was accomplished with a distilled water mobile phase at a flow-rate of approximately 5 ml/min and an average pressure of 150 p.s.i. The time of analysis under these conditions was approximately 7 min. A typical chromatogram is shown in Fig. 1. To determine the nitric-to-sulfuric acid ratio (N/S), the integrated area of nitric acid was multiplied by a response factor and divided by the area of sulfuric acid. The response factor was determined by chromatographing synthetic acids having N/S ratios normally encountered.

RESULTS AND DISCUSSION

Although nitric and sulfuric acids could be separated and determined as separate entities by the LC method, it was felt that better control over mixed acid composition could be obtained by calculating the results as the N/S ratio. The use of the N/S ratio simplified the analysis by making it unnecessary to inject exact reproducible amounts of sample into the liquid chromatograph. This was made possible by the

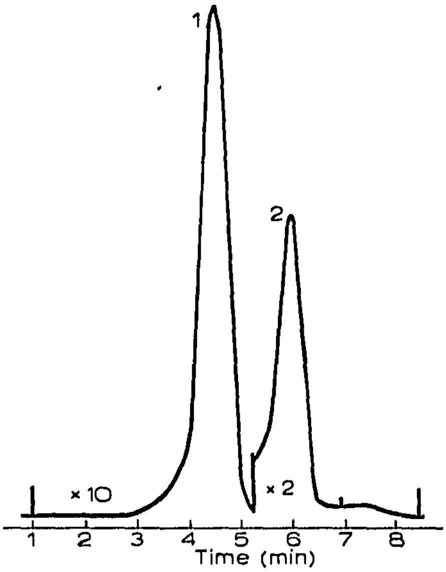

Fig. 1. LC separation of sulfuric (1) and nitric (2) acids.

fact that sulfuric acid (oleum) is added at only one point in the nitration process, *viz.* the last nitrator, and therefore acts essentially as an internal standard in the LC method. Also, by using the N/S ratio, interference by dissolved or entrained nitrotoluenes is avoided.

The precision of the LC method was first investigated by repeated analysis of a single acid sample. The data indicate excellent replication of N/S values with a

TABLE I

N/S VARIABILITY AS A FUNCTION OF TIME FOR AN INDIVIDUAL NITRATOR

Time (min)	*N/S ratio*
0	0.1399
5	0.1333
10	0.1347
15	0.1378
20	0.1335
25	0.1378
30	0.1343
35	0.1389
40	0.1426
45	0.1403
50	0.1359
55	0.1413
Average	0.1375
Range	0.0093
Standard deviation	0.00317
Coefficient of variation, %	2.30

TABLE II

PER CENT HNO_3 *VERSUS* N/S RATIO

Nitrator 1A		*Nitrator 1B*		*Nitrator 2*		*Nitrator 3A*		*Nitrator 3B*		*Nitrator 4*		*Nitrator 5*		*Nitrator 6*	
HNO_3 (%)	*N/S*	*HNO_3 (%)*	*N/S*	*HNO_3 (%)*	*N/S*	*HNO_3 (%)*	*N/S*	*HNO_3 (%)*	*N/S*	*HNO_3 (%)*	*N/S*	*HNO_3 (%)*	*N/S*	*HNO_3 (%)*	*N/S*
3.5	0.1140	4.4	0.1253	6.0	0.1379	9.5	0.2080	8.7	0.1724	11.0	0.1956	13.0	0.2417	14.5	0.2554
4.6	0.1330	4.3	0.1040	5.5	0.1590	10.3	0.2323	9.1	0.2154	11.7	0.2380	14.3	0.2663	14.8	0.2608
4.6	0.1473	4.0	0.1257	6.2	0.1713	9.3	0.2410	8.3	0.2019	11.6	0.2105	13.7	0.2704	14.2	0.2661
3.5	0.0789	3.6	0.1422	5.0	0.1341	9.4	0.2032	6.0	0.1608	11.2	0.2285	13.8	0.2652	14.0	0.2645
4.5	0.1294	3.0	0.0772	5.3	0.0887	9.8	0.2061	9.1	0.1980	11.3	0.2103	13.5	0.2436	13.8	0.2629
4.6	0.1196	4.3	0.1237	5.4	0.0895	12.4	0.2600	10.9	0.1980	14.0	0.2026	15.1	0.2070	16.7	0.2770
4.4	0.1413	4.0	0.0976	6.3	0.1670	11.1	0.2278	8.1	0.1834	13.2	0.2445	14.9	0.2450	16.6	0.2649
4.1	0.1174	3.7	0.1012	5.2	0.1233	9.5	0.1780	8.0	0.1296	12.1	0.2196	12.2	0.2323	15.3	0.2495
4.3	0.1121	3.9	0.1013	5.7	0.1264	10.1	0.2075	8.5	0.1883	11.8	0.2184	12.8	0.2362	13.3	0.2400
4.8	0.1063	3.8	0.0893	6.2	0.1096	10.8	0.1975	8.8	0.2184	11.6	0.2454	13.0	0.2337	13.0	0.2326
Average															
4.39	0.1199	3.90	0.1088	5.68	0.1307	9.21	0.2161	8.55	0.1861	11.95	0.2213	13.63	0.2441	14.62	0.2574

coefficient of variation of 0.25%. The instrumental variation plus the sampling variation was 1.58% as determined by taking replicate acid samples from a nitrator. This precision compares favorably with that of the titration method, which has a coefficient of variation of 4.68%. Various water-to-acid dilution ratios in the range of 3:1 to 10:1 were investigated and showed that dilution did not adversely affect the precision of the method. The lower coefficient of variation of the LC method is caused in part by the fact that the LC results are unaffected by the amount of nitrotoluenes in the sample taken for analysis.

The applicability of the N/S ratio for process control was evaluated by determining the variability of the ratio in a single nitrator under stable operating conditions. A sample of nitrating acid was removed every 5 min during a 1-h period. The N/S ratio was determined on these samples and the results are shown in Table I. The 2:30% coefficient of variation indicates that the N/S ratio remains fairly stable with constant feed rates.

The use of the LC technique was further evaluated on an operating TNT line by monitoring the N/S ratio of all nitration vessels and comparing the ratios with the nitric acid value as determined by the ferrous ammonium sulfate technique. The data presented in Table II show some inconsistencies because the titration results were not corrected for soluble or entrained nitrotoluenes. Correlation of the nitric acid titration results and N/S ratios led to selection of N/S ratios for control of nitric acid in each vessel on the operating line.

In the upper nitration stages, where the total acidity is approximately 100% or above, the N/S ratio is the sole control on acid composition, and adjustments are made in the nitric feed to each vessel with a constant feed of oleum into the last nitrator. In the mono- and dinitration stages, where water is added to control the rate of reaction, total acidity as measured by acid density is the primary control, with nitric acid feed being secondary to obtain the desired N/S ratio. One trinitrotoluene line was operated using these criteria and the selected ratios, with a noticeable improvement in control of nitric acid concentration in all vessels.

The success of the rapid off-line LC approach to control of the nitration process has led to the decision to investigate instrumentation for on-line analysis, particularly since process liquid chromatographs are now commercially available.

ACKNOWLEDGEMENTS

The authors express their gratitude to A. A. Nixon for development of data. The work was supported by the Manufacturing, Methods and Technology Division, Picatinny Arsenal, Dover, N.J., U.S.A.

REFERENCES

1 J. Kohlbeck, C. Chandler and W. Bolleter, *J. Chromatogr.*, 46 (1970) 173.
2 C. Chandler, J. Kohlbeck and W. Bolleter, *J. Chromatogr.*, 64 (1972) 123.
3 C. McKinney, Jr., W. Rogers and W. McNabb, *Anal. Chem.*, 19 (1947) 1041.
4 N. H. Furman (Editor), *Scott's Standard Methods of Chemical Analysis*, Vol. 11, Van Nostrand, New York, London, 5th ed., 1939, p. 2217.
5 Work performed in these laboratories.
6 J. Ridden, R. Barefoot and J. Roy, *Anal. Chem.*, 43 (1971) 1109.
7 J. Schmit and R. Henry, *Chromatographia*, 3 (1970) 497.
8 P. Neddermeyer and L. Rogers, *Anal. Chem.*, 40 (1968) 755.