

TECHNICAL NOTE
INTERLABORATORY CALIBRATION OF PEROXYACETYL
NITRATE LIQUID STANDARDS

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Abstract—Peroxyacetyl nitrate (PAN) solutions in the concentration range 10–100 μg PAN per ml solvent were distributed and analyzed by ten European laboratories. Overall precision accounting for standards' preparation, transport, storage and analysis resulted in standard deviations of $16 \pm 8\%$ of the mean for the high- and $25 \pm 8\%$ for the low-end of the concentration range. Following alkaline PAN hydrolysis, nitrite anions were determined, mostly by chemically suppressed ion chromatography, with better precision than the acetate anions.

Key word index: PAN alkaline hydrolysis, PAN hexane solutions, ion chromatography, nitrite and acetate anions determination.

INTRODUCTION

Peroxyacetyl nitrate (PAN) is an important constituent of photochemical pollution. Unlike ozone, PAN has only tropospheric sources and could therefore be a better indicator of photochemical pollution (Penkett *et al.*, 1977; Nieboer and Van Ham, 1976). However, PAN is not used as extensively as ozone, because of the difficulty in its analysis and particularly in the calibration of the electron capture detector (ECD). The difficulty associated with the calibration is due to the thermal instability of PAN and thus certified standards cannot be produced, stored and distributed in a normal way.

There are two categories of PAN calibration procedures depending on the method of PAN synthesis. When PAN is prepared in the gas phase, calibration is also carried out in the gas phase. When PAN is prepared in the liquid phase, then calibration can be carried out either in the liquid or in the gas phase. Both categories have their advantages and disadvantages, which, on many occasions, are subjective. An important factor is the experience of a laboratory to work with gases or liquids, which in turn frequently may be the result of the available instrumentation. In early studies, PAN

was prepared in the gas phase (Stephens, 1969; Gay *et al.*, 1976), and the calibration was also carried out in the gas phase using infrared techniques (Stephens, 1969; Stephens and Price, 1973). Additional gas-phase synthesis and calibration in the gas or liquid phase continued to appear in the literature (Lommeman *et al.*, 1982; Grosjean *et al.*, 1984; Schurath *et al.*, 1984; Joos *et al.*, 1986; Warneck and Zerbach, 1992).

Because of the convenience in handling liquids, a PAN synthesis in the liquid phase was sought (Kravetz *et al.*, 1980; Louw *et al.*, 1975). The major thrust in the liquid PAN synthesis was given by the studies of Nielsen *et al.* (1982) and Gaffney *et al.* (1984), who reported improved and convenient liquid-phase PAN preparation methods.

This work presents the results and the experience gained of the first PAN interlaboratory calibration ever performed. The goal was to determine PAN with a precision of $\pm 10\%$. Attainment of this goal would constitute a major step in the reliable calibration of the ECD.

PROCEDURES

The Norwegian Institute for Air Research (NILU) prepared the standards and coordinated their distributions to

Table 1. Results of first distribution, values are µg PAN per ml hexane

Laboratory	Date	IC instrument, column and eluant	A				B				C				D		NPN		
			IC/Ac	IC/nitrite	Salzman	CSV	IC/Ac	IC/nitrite	IR	Salzman	IC/Ac	C/nitrite	Salzman	IC/Ac	C/nitrite	Salzman		IR	IC/Ac
Lab. 1	27&28.11.91	Dionex, AS4A, borax	98.3	100.2	10.7														
Lab. 2	12.11.91	Dionex, AS4A, borax	129.8	93.2															
Lab. 2	29.11.91	NaHCO ₃ /Na ₂ CO ₃	121.3	92.8															
Lab. 2	12.11.91	Dionex, AS4A, borax	87.9	94.2															
Lab. 3	11.11.91	Dionex 40001, AS3, NaHCO ₃ /Na ₂ CO ₃	93.9																
Lab. 3	11.11.91	Dionex 40001, AS3, NaHCO ₃ /Na ₂ CO ₃	104.7																
Lab. 4	11.12.91	Wescan, Vydac 302 IC Phthalic acid																	
Lab. 5	07&11.11.91	Dionex 45001, AS4A, borax																	
Lab. 5	01&02.12.91	NaHCO ₃ /Na ₂ CO ₃																	
Lab. 6	09.12.91	Dionex 2010, AS4A, NaHCO ₃ /Na ₂ CO ₃	98.3																
Lab. 6	09.12.91	Dionex 2010, AS4A, NaHCO ₃ /Na ₂ CO ₃	84.4																
Lab. 7	19.12.91	Dionex, AS3																	
Lab. 7	19.12.91	Dionex, AS3																	
Lab. 8	13.11.91	NaHCO ₃ /Na ₂ CO ₃																	
Lab. 8	13.11.91	Dionex 2010, AS4A, borax	112.4																
Lab. 8	13.11.91	Dionex 2010, AS4A, borax	149.2																
Lab. 9	04&05.11.91	Dionex 2010, AS4A, borax	109.6																
Lab. 9	04&05.11.91	Dionex 2010, AS4A, borax	107.0																
Lab. 10	10.12.91	Dionex, AS4, Borax	113.9																
		Average	113.9	90.0	116.3	93.6	13.9	10.7	14.3	10.8									
		Standard deviation	17.2	7.6	22.2	9.0	7.8	3.3	7.2	3.3									
		Stand. dev. in % of average	15.1	8.5	19.1	9.6	56.1	31.3	50.3	30.5									
		Average	95.9		6.1				11.1	9.7									
		Standard deviation	1.3	1.0	12.6	11.1			4.3	11.6									
		Stand. dev. in % of average	1.3	1.0	12.6	11.1			4.3	11.6									

Statistics without accounting for eliminated values
Average
Standard deviation
Stand. dev. in % of average

Laboratory numbers different from author listing sequence.

Table 3. Results of third distribution, values are $\mu\text{g PAN}$ per ml hexane

Laboratory	Date	Eluant	A			B					
			IC-Ac $\sigma\%$	IC-nitrite $\sigma\%$	Saltzman Ave.	IC-Ac $\sigma\%$	IC/nitrite $\sigma\%$	Saltzman Ave.			
Lab. 1	30.6.93		4.2	92.2	2.2	103.5	6.3	99.3	3.9	107.7	
Lab. 2	15&16.07.93 09.08.93 08&09.11.93	Borax eluant $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ Borax	4.6	102.3	4.8	98.8 94.7 79.0	1.8	104.5	3.0	102.2 96.0 84.8	
Lab. 3	25.11.93	$\text{NaHCO}_3/\text{Na}_2\text{CO}_3$			7.3	100.7			12.4	111.1	
Lab. 4	02.12.93	Phthalic acid	5.2	115.5			6.3	139	2.8	110	
Lab. 5	23.07.93 23.07.93 01&07&31.10.93	Borax eluant $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ Borax eluant	17.0	103.4	3.0	84.1 83.9 107.5	9.1	87.0	9.0	82.3 94.1 110.2	
Lab. 6	2&26&31.10.93 24&25.11.93	$\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$				87.0 85.0				91.0 92.0	
Lab. 7	31.10.93	Borax	4.2	98.4	2.0	113.1	4.5	99.5	5.9	114.0	
Lab. 8	29.09.93		4.2	90.0				98.4			
Lab. 9	31.10.93		11.1	115.0	0.7	110.5	IR 11.3	4.2	117.5	9.3	122.0
Lab. 10	09.07.93 01.09.93							113.0 115.1		117.0 115.2 115.5	
Average				98.0		95.7		101.6		101.3	
Standard deviation				13.7		11.7		19.5		12.2	
Stand. dev. as % of average				13.9		12.2		19.2		12.1	

Statistics without accounting for eliminated values

Average

Standard deviation

Stand. dev. in % of average

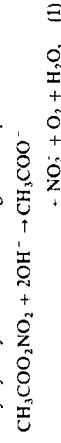
the ten participating laboratories mentioned in the affiliations given for this paper. To thermally preserve the standards, NILU placed them in glass vials surrounded by 12 kg of dry ice in a styrofoam insulated plywood box, certified for air transport of dangerous goods. This packing assured that the solutions would be kept at dry ice temperature for approximately 4 d. Only three of the 50 transports suffered serious delays, and one was lost.

Three distributions took place in a period of 2 yr: in the first the PAN concentrations determined by the coordinator were made known to the participants; in the following two the coordinator gave a $\pm 30\%$ interval of the expected PAN concentration. The true PAN concentration was defined as the mean of the results reported by all participants, after the exclusion of the outliers due either to analysis errors or to sample destruction.

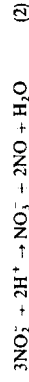
Each time six PAN standards were distributed. Solution A contained PAN and *n*-propyl nitrate (NPN), each around 100 μg (PAN nominal value) per ml of solvent (hexane). NPN was added as an internal standard. Solution B contained around 100 μg PAN per ml solvent, solution C contained PAN and NPN, each around 10 μg per ml solvent. Solution D contained around 10 μg PAN per ml, solution E contained around 100 μg NPN per ml and the last solution contained only hexane. The stock PAN was synthesized according to the procedure of Nielsen *et al.* (1982). Prior to preparation of the standards, a portion of the stock PAN was HPLC purified with the collection bottle cooled at -20°C . The hexane solvent was also HPLC purified. The standards were first analyzed by the coordinator before distribution, then analyzed by each participant soon after reception, reanalyzed by each participant prior to their return to NILU (usually two months after their reception) and reanalyzed by the coordinator after their return to him. This schedule, in addition to the determination of

the PAN concentrations, allowed for the derivation of valuable information with regard to storage and handling of the solutions by the individual laboratory and the effect of transport.

The analytical methods used in the PAN determination were chemically suppressed ion chromatography (IC), practiced by all laboratories except laboratory 10, which used the method only in the first distribution, and laboratory 4, which used electronically suppressed ion chromatography. Additional analytical techniques such as Fourier transform infrared (FTIR), the spectrophotometric Saltzman method and cathodic stripping voltametry (CSV) were also used by some participants. In order to apply these methods PAN was hydrolyzed in a 25 mM NaOH solution, laboratories 2, 3 and 10 used 10, 20 and 50 mM NaOH solutions, respectively. In the third distribution, laboratory 3 also used 50 mM NaOH solution. The choice of the alkaline solution was very important as the following conditions had to be met: completely hydrolyze PAN according to the equation:



provide a pH which would prevent the oxidation of nitrite anion into nitrate anion, according to the equation



and simultaneously the alkalinity should not seriously disturb the ion chromatograph's baseline. This last factor is particularly important when the nitrite peak elutes very early, as is the case with the eluant $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ and column ASMA. Alkaline hydrolysis thus allows for the determination of PAN from the stoichiometry of a above reactions via the equation:

$$[\text{PAN}] = [\text{CH}_3\text{COO}^-] = [\text{NO}_2^-] + 3[\text{NO}_3^-] \quad (3)$$

C				D				100 µg NPN per ml				
IC/Ac σ% Ave.	IC/nitrite σ% Ave.	Saltzman	IC/Ac σ% Ave.	IC/nitrite σ% Ave.	Saltzman	IC/Ac σ% Ave.	IC/nitrite σ% Ave.	Saltzman	IC/Ac σ% Ave.	IC/nitrite σ% Ave.	Saltzman	
4.2	10.0	2.4	12.1	13.3	9.4	12.3	11.9		6.4	1.2	0.0	
0.0	10.3	3.0	11.0	3.1	10.9	6.1	11.1			2.6		
	10.3		7.9		11.8		10.1	11.1				
		10.0	10.2		10.2		8.2				0.0	
						1.0	10.5			0.0	0.0	
7.0	22.1			3.7	20.3	14.3	22.3			0.0		
13.8	10.6	3.9	9.8	27.7	11.8	4.5	9.8					
		14.4	9.5		9.2	9.8	9.8					
5.5	9.2	6.3	12.9	3.6	8.4	0.0	13.5					
							13.0				0.0	
							12.0					
							11.8					
9.3	10.8	4.2	11.8	13.9	11.5	4.1	12.3		100.0	0.8	0.1	
	11.9				11.9							
10.5	15.5		13.8	IR127	18.5	14.5	14.6	15.5	IR11.9	32.6	2.0	0.0
				13.2					12.7			0.0
				13.7					13.0			
12.3			10.9		12.1		12.3			1.1		
4.1			1.7		3.5		3.6			1.0		
33.3			15.9		29.1		28.9			7.6		
11.1					11.1		11.5					
1.9					1.9		2.0					
17.5					16.7		17.2					

During the course of this study, however, it was decided not to include the concentration of nitrate anions in the calculation of the PAN concentration. A high nitrate anion concentration indicates a not sufficiently alkaline solution, with the possible consequence that PAN is not quantitatively hydrolyzed. The concentration of NO_3^- should be very low because the distributed PAN was HPLC purified. Laboratories 1 and 7 found the nitrate anion concentration to be reasonable at 5-15% of the NO_2^- concentration. Laboratory 1 showed that hydrolysis with NaOH solution of concentrations varying from 3 M to 25 mM yielded the same results.

Equation (1) shows that the PAN determination can be based either on the measurement of the concentration of nitrite or acetate anions. In chemically suppressed ion chromatography the nitrite anions can be determined either with eluant $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ or with eluant borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), in which case also the acetate anions can be determined, using column AS4A with guard precolumn AG4A. The used columns are shown in Table 1.

RESULTS AND DISCUSSION

First distribution

In this distribution the PAN concentrations determined by the coordinator were made known to the participants. As shown in Table 1, the PAN concentration based on the acetate anion determination was larger than the respective values based on nitrite anion concentration, even when the very high PAN concentrations reported by laboratories 9 and 2, due most probably to acetate anion contamination, were excluded. Furthermore, the higher average PAN concentrations obtained by the whole group compared to the respective values based on the analysis of nitrite anions could

also indicate a minor acetate anion contamination, if it were ascertained that the nitrite anion concentration were not low for another reason, e.g. oxidation to nitrates. The variability shown from the standard deviation (expressed as percent of the average) was also greater for the results derived from the acetate compared to the nitrite analysis. In addition, in Table 1 are given the statistics when outliers, shaded cells, were eliminated using the Q -test at the 90% confidence level.

Second distribution

The results are shown in Table 2. With a few exceptions, no results for PAN based on acetate anion analysis were reported. The participants had obtained much higher PAN values when based on the analysis of acetate anions than on nitrite anions. It was inferred that an acetate anion contamination had occurred at the coordinator's laboratory during preparation of the standards. A probable contamination source may have been the acetic acid used in the priming stages of the PAN HPLC purification procedure (Bredeweg *et al.*, 1979). The analysis of the PAN standards soon after reception and just before return to the coordinator showed that laboratory 2 could have a storage problem, as also indicated by the results of the following third distribution. During this study it was verified that PAN standards cannot be stored at temperatures above -20°C ; at temperatures around -30°C PAN standards were safely preserved for at least three months.

Third distribution

With the experience gained through the past two distributions the third one was more successful, as shown in Table 3. In addition to the average PAN values, the standard deviations expressed as percent of the average, SDAFV, were also reported by each laboratory. The differences in the PAN

concentrations based on the analysis of acetate and nitrite anions were in this round very small. With all data considered the SDAPAV ranged from 12.1 to 19.2% for solutions A and B and from 15.9 to 33.3% for solutions C and D. The outliers, shaded cells, were determined by the *Q*-test when the number of data were less than ten and the *T*-test when the number of data were more than ten, both at the 90% confidence level. When the outliers were eliminated the SDAPAV for solutions C and D was reduced to 15.9–17.5%. During this last distribution it was verified, based on the results of laboratory 2, after reception of standards from the coordinator and prior to their return to NILU, that partially destroyed PAN would still give high acetate anion concentration while nitrite anions would better represent the condition of the sample. The low PAN values derived from acetate analysis reported by laboratory 5 were associated with low acetate anion calibration factors. The acetate anion calibration factors varied significantly more than the respective ones for the nitrite anions.

CONCLUSIONS

This work has demonstrated that it is possible to prepare, distribute, store and analyze by a large number of laboratories, PAN standards in the concentration range 10–100 µg PAN per ml solvent using IC determination of nitrite and acetate anions. The obtained standard deviations were equal to $16 \pm 8\%$ of the average for the high- and $25 \pm 8\%$ for the low-end concentration range. When the statistically rejected values were not considered the respective values became $16 \pm 8\%$ and $12 \pm 8\%$. The determination of the nitrite anion was found to be the preferred method, provided that no nitrite anions were oxidized to nitrate anions. A sodium hydroxide solution in the concentration range 25–50 mM fulfilled the above condition. An additional advantage in using the analysis of nitrite anions is that no HPLC purification of PAN is required. Acetate anion determinations, initially considered to be the preferred method, were proved to be less reliable because of ease of contamination, large calibration variabilities and because partially decomposed PAN still gave substantial amounts of acetate anions. In addition to IC, other analytical techniques, although much less used in this intercalibration, such as the Saltzman nitrite colorimetric analysis, cathodic stripping voltametry determination of nitrite anions and FTIR were also shown to yield reliable results. The results of the present study have indicated that centrally distributed liquid PAN standards can reliably be used in PAN monitoring on national or European networks.

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