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Contract EV4V-CT90- 0222

Peroxy Acetyl Nitrate Intercalibration

**Progress Report no 3
1 May to 31 December 1993**

**Co-ordinator:
Terje Krognæs**



**NORSK INSTITUTT FOR LUFTFORSKNING
Norwegian Institute for Air Research
POSTBOKS 64 — N-2001 LILLESTRØM — NORWAY**

Contract EV4V-CT90-0222
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Co-ordinator's overview

Progress reports from all the contractors and associated contractors are included on the following pages. Also some informal partners contribute actively. KFA Jülich has co-operated with Meteorologieconsult. The JRC Ispra does not receive financial support through the project contract, but is active.

The project was originally scheduled to be completed by 31 April 1993, but was prolonged to 31 December 1993. Further delay has occurred during the prolongation period. The last scheduled distribution of PAN standards (CAL.III) has been cancelled. The amount of data available from the three distributions that have been performed (PREP.III, CAL.I and CAL.II) is large enough to fulfil the purpose of the experiments. The accuracy of the results are higher than expected in spite of the technical problems that have been experienced.

CAL.II

New PAN solutions were purified by HPLC and distributed to the participants after the summer holidays. Precautions were made to avoid acetic acid contamination. The participants performed ion chromatographic analysis of the PAN concentration in the solutions shortly after arrival and (most participants) before returning samples to the co-ordinator. The "true" concentrations (best values obtained by the co-ordinator) were not given to the participants. Instead, nominal concentrations with $\pm 50\%$ tolerance were specified.

The participants completed their calibrations and returned samples of the solutions to the co-ordinator in December 1993 and January 1994. The re-calibration of the samples was performed in January 1994.

Ambient PAN Monitoring

Due to various technical difficulties the monitoring programme in 1992 did not include all participants. From 1993 a somewhat more complete data material is available. Local PAN monitoring programs are rather normal. However, it is difficult to compare results from different countries due to the uncertainties of the PAN calibration methods.

During the the STEP PAN intercalibration project the participants have had access to identical PAN solutions. This is a first pre-requisite for comparing the monitoring results. There are two other significant error sources to consider.

Different methods for calibration of the PAN instruments may give different results even if identical PAN solutions are used. Furthermore, different PAN instruments may be more or less sensitive to differences in the matrix of the calibration gas and the ambient air. The last two effects are outside the scope of the present intercalibration project, but may influence the results of the monitoring programme.

Further work

The project is now formally finished, but some data evaluation and reporting still remains to be done. The participants will complete the work without further economic support from the CEC. The reports are now scheduled to be completed in May 1994 (schedule outlined in letter to DG XII/D-1 dated 24 February 1994).

Participant no 1

NILU

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EV4V-CT90-0222
Peroxy Acetyl Nitrate intercalibration
Progress report no 3
Terje Krognnes
February 1994

WORK PERFORMED AND RESULTS OBTAINED

The standards distributed in phase CAL.I were returned to the co-ordinator and re-analyzed in the end of the second reporting period. In the beginning of the present reporting period (May to June 1993) analysis of the returned CAL.I samples were repeated after improvement in the analysis method.

NILU prepared PAN solutions for the CAL.II distribution. A PAN solution was purified on HPLC and calibrated by ion chromatography. Pure hexane was also passed through the HPLC to create a reference for infrared absorption methods. Care was taken to avoid acetic acid contamination in the solution. The solution was diluted and divided, and a stable component NPN (n-propyl nitrate) was added to some of the resulting solutions. The solutions were again calibrated by ion chromatography and filled on small bottles. The bottles were distributed to the participants packed in dry ice.

Samples of the distributed solutions were returned to NILU in December 1993 and January 1994. All returned samples were re-analyzed by ion chromatography. The results were again more uniform than could be expected, with the exception of some outliers in acetate determination. In the previous distribution of solutions (CAL.II) such outliers were caused by a contamination accidentally added by the co-ordinator. In the last distribution (CAL.II) no such simple explanation can be seen. These observations reinforce the overall impression that unknown error sources are still significant in the acetate analysis. Calibrations based on nitrite/nitrate analysis seem to yield more reliable results.

Nilu did not monitor ambient PAN in 1992 due to instrument malfunction. In 1993 a monitoring program was performed at the station Birkenes at the southern coast of Norway. Due to continued technical difficulties in some periods, data are missing for days with rain or very high humidity.

FURTHER WORK

NILU will complete the technical reports and take part in a final project meeting. There, the group will correct any irregularities in the draft reports and agree on the best way of producing the final publications.

Participant no 2

University of Paris XII

Progress report N°3 on activities May-Dec 93

Call II experiment have been performed by Ion Chromatography without any particular problem. Acetate ion and nitrite ions have been used both for the calibration.

| | PAN | cal/AcO ⁻ ion | cal/NO ₂ ⁻ ion |
|---------------|-------------------|--------------------------|--------------------------------------|
| Results are : | PAN 100 µl/ml | 139 µl/ml | 110 µl/ml |
| | id + NPN 100µl/ml | 115,5 µl/ml | |
| | PAN 10 µl/ml | 20,3 µl/ml | 22,3 µl/ml |
| | ID + NPN 10µl/ml | 20,3 µl/ml | |
| | NPN 100µl/ml | 0 µl/ml | |

During the period, PAN has been measured on the field at Porspoder (Bretagne) with the objective of determining the composition of PAN in the marine atmosphere. The improvement in the detection limit of our automatic PAN analyser, performed by the end of the previous period, has been very efficient and we have been able to record a long series of significant data in the low concentration range. Only some percent of the time, the concentration downs under 10 pptv. The annual variation of PAN in the eastern atlantic marine atmosphere is now available with an good accuracy and good absolute calibration.

G. TOUPANCE



Participant no 3

University of Patras

PART B. DETAILED REPORT OF THE CONTRACTORS AND SUB-CONTRACTORS

Contractor : University of Patras
Department of Chemistry
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I. OBJECTIVES FOR THE REPORTING PERIOD:

To analyze the distributed by NILU PAN standards of phase CAL II.

III. MAIN RESULTS

PAN INTERCALIBRATION.

We analyzed the distributed PAN standards of phase CAL II at two different time periods. First when we received the standards, July-August 1993 and second when we shipped back the standards to NILU, October 1993. In July-August we determined the PAN content of the standards from the determination of nitrite anions by IC on the AS4A column with eluants $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ and borax and from the determination of acetate anions with the eluant borax. Unfortunately in October our column had deteriorated so much that we could not use it for the analysis of NO_2^- with eluant $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ even with the use of the Dionex On-Guard H 39596 filters.

Thus in October we determined the NO_2^- and acetates using only borax as eluant. The obtained results are shown below:

Results of analyses of second PAN intercalibration, $\mu\text{gPAN/ml}$ hexane.

| Standard | Analysis time | Acetates | Nitrates | Nitrates |
|----------|---------------|------------------------|-----------------------|--|
| | | Eluant | Borax | Eluant $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ |
| A4 | July | 103.4($\sigma=17.6$) | 84.1($\sigma=2.5$) | 78.6($1\sigma=13.2$) |
| | October | 70.8($\sigma=12.6$) | 107.5($\sigma=5.8$) | - |
| B4 | July | 87.0($\sigma=7.6$) | 83.0($\sigma=7.1$) | 94.1($\sigma=3.5$) |
| | October | 67.8($\sigma=3.6$) | 110.2($\sigma=3.2$) | - |
| C4 | July | 10.5($\sigma=1.3$) | 9.8($\sigma=0.4$) | 9.5($\sigma=1.3$) |
| | October | 9.2($\sigma=0.5$) | 12.4($\sigma=0.2$) | - |
| D4 | July | 11.8($\sigma=3.1$) | 9.8($\sigma=0.4$) | 9.8($\sigma=0.8$) |
| | October | 8.4($\sigma=0.3$) | 13.5($\sigma=0$) | - |
| NILU'S | | | | |
| Hexane | | 0 | 0 | 0 |

As shown in above table all methods yielded very good results for the data obtained in late July, the results agree to within $\pm 5-10\%$. The results obtained from the analyses of acetates carried out after almost two months storage in a household freezer at -35°C , show that the PAN content of the standards has remained the same within the experimental uncertainty. The results however of October based on the nitrite analysis show a significant increase of the nitrite equivalent PAN content, which is significantly larger than the experimental uncertainty. We can only speculate on this increased nitrite content of the standards. Maybe there was a nitrite contamination of the standards or the employed glassware etc.

AMBIENT PAN MEASUREMENTS

In order to make sure that the observed peak of ambient air chromatogram was due to PAN, we injected into the GC PAN prepared by NILU or by ourselves. The identity of the retention times was a prerequisite in order to assign the observed peak to PAN. This condition was always met by our data. An additional check of the identity of the peak that we assign to PAN was carried out either by heating approximately one meter of the ambient air, inlet tubing to the GC to 250°C, or by heating the ECD detector to 150°C. If the peak were PAN it was destroyed as expected. This check was carried out on the average of one time per day. On some occasions however and especially with the data of March 1993 the peak we believed from its retention time to be PAN was not thermally destroyed. At that time we interrupted the automatic sampling and analysis with the HP-1 wide bore column and switched to a 60cm long 1/8" O.D. packed column filled with 4.8% QF-1 and 0.18% diglycerol on 80/100 mesh chromosorb G, which we had successfully used in the past for the measurement of PAN. Although we injected larger amounts of air, up to 5 ml, than in the wide bore column, 1 ml of air, the PAN peak was barely seen. In order to improve the sensitivity of our method we cryoconcentrated ambient air, in a procedure similar to the one described by Glavas and Schurath (*Chimika Chronika New Series*, 12, 89-97(1983)). Approximately four samples per day were obtained with this manual labour intensive method from 23-29 August 1993. The PAN values obtained with the cryoconcentration were approximately two times higher than the values obtained in the respective time period of August 1992 and from the subsequent ambient values of PAN with the HP-1 wide bore which was again installed in the GC and kept in operation until 7 September 1993. The final analysis of the ambient PAN data will be carried out after the final meeting of the program, when a decision is expected to be taken as to the fate of the ambient air PAN data.

Participant no 4

TNO

Progress Report STEP PL 900289 "PAN INTERCOMPARISON"

J.C.Th.Hollander, TNO-Environmental Sciences

P.O. Box 6011, 2600 JA Delft, The Netherlands

Following the trial intercomparison (PREP III) and the first (CAL I) intercomparison, a second (CAL II) intercomparison was carried out. As before it included the analyses of standard solutions distributed by the coordinator and solutions synthesized in our laboratory by FTIR and ion chromatography of acetate and nitrite after hydrolyses.

The results of the CAL II exercise in our laboratory were satisfactory to the extent that the variance between the results of the three different analytical methods (expressed as a relative standard deviation) ranged from 2 to 13%, which was a slight improvement as compared to earlier exercises.

There are, however, some critical remarks to be made too, which mainly concern the analyses of the products of the hydrolyses of the PAN standards.

The ion chromatographic analyses produces incidentally outlying results which are only detected because in the intercomparison exercises both acetate and nitrite are analysed in several aliquots of different solutions with nominal equal concentrations of PAN.

The calibrations of the IC show significant drift with time for both acetate and nitrite which may be the result of instrument performance or sample stability.

The analyses of acetate produces rather variable unacceptable high blanks the origin of which are difficult to trace.

The molar ratio of acetate to nitrite is generally higher than the expected theoretical value of one.

The specific adsorption coefficients used for quantitation of PAN by FTIR of the liquid phase have not been established firmly. They are in fact based on the gas phase adsorption coefficients given by Stephens which were criticised in more recent work by Tsalkaní and Toupance.

From the results obtained in our laboratory we therefore conclude that IC analyses of acetate and nitrite is rather laborious and does not produce reliable results. Moreover this method gives no information on the quality of the PAN standards. The FTIR analyses on the other hand, simultaneously provides qualitative and quantitative information on the standard solutions and works handsomely. Presently its main draw back is the absolute value of the quantitation.

Ambient PAN measurements, which started in July 1991, were continued during 1993. The results up to 1992 have been worked out and made available to the participants of the project. Those of 1993 will follow soon. A summary table showing the periods for which data are missing has also been presented.

Participant no 5

Meteorologie consult gmbh

**Progress Report for the period May 1993 - Dec. 1993.
Meteorologie Consult GmbH**

The latest PAN/HEXANE-solution was calibrated successfully using Ion Chromatography. We have finally modified our new dynamic PAN calibration device. The dynamic range for PAN concentrations ranges between ca. 100 ppt an some ppb. Primary gas is a 10 ppm NO premixture in nitrogen. Two PAN GCs with capillary columns were operated for several months in Frankfurt under low winter PAN concentrations. The two devices show an excellent correlation. Our PAN-measurements under clean air conditions in the free troposphere on the Canary islands (Staion IZANA) continued. Here the static and the new dynamic calibration device were compared. The efficiency of the calibration procedure was tested using an NO/NOx/NOy analyzer. The efficiency of the calibration method was further tested with a modified Saltzman method. Using a chemical model, the efficiency of the reaction was calculated under the conditions of the reactor.

Dr. Rainer Schmitt

| | | | |
|------------------|--|----------------|--|
| NILU | | | |
| Meldet: | | U-91051 | |
| 9/2-94 <i>RS</i> | | | |
| Festmetel: | | Saksbehandler: | |
| <i>RS</i> | | <i>TK</i> | |
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Participant no 6

ARD (name now changed to ITM)

STEP PAN INTERCALIBRATION PROJECT

Contract EV 4V-CT90-0222

PROGRESS REPORT Nr 3

*R.Romero and P.Oyola
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Report of activities in the STEP PAN-Intercalibration project, carried out by the Air Pollution Laboratory (APL), period between 1st May and 31st December 1993.

1.- In-situ calibration and comparison between two different calibration methods of the PAN-analyzer.

Until now, the calibration of PAN-instrument at Studsvik, has been made by injection of gaseous dilution of liquid PAN standard (previously diluted in Tedlar bags). Now, the accuracy of the PAN-analyzer for measurement of PAN, has been tested using this common calibration method vs an alternative system based on the diffusion principle, where liquid PAN solution is diffused through a very thin glass calibration tube. Then, the gas-phase PAN standard is parallel injected in two different instrument: a Chemiluminescence NO-Analyzer (Eco-Physics al-ppt) previously connected to a NO₂ --- > NO-converter (Master Blaster) and into the PAN-analyzer.

2.- Participation in an All Nordic Measurement Campaign.

During 15th February and 30th June 1993, unattended PAN measurements were carried out by routine monitoring at the Aspvreten station in Sweden. According to a Nordic agreement, as a first step towards harmonisation of PAN measurement within the Scandinavian countries participating at the EUROTRAC-TOR project (Tropospheric Ozone Research).

Participant no 7

CNR

PROGRESS REPORT ON THE ACTIVITY CARRIED OUT BY THE I.I.A.-C.N.R.
FROM MAY 1993 TO DECEMBER 1993 IN THE FRAME OF THE STEP PROJECT-
PAN INTERCALIBRATION.

P. CICCIOLO

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Monterotondo Scalo- ITALY

The methodology for calibrating ECD-based PAN-Analyzers has been established by using the Standard solutions provided by the Coordinator. PAN was quantified by ion-liquid-chromatography after alkaline hydrolysis by measuring the nitrite ion. GC was used to determine the PAN/NPN response factor. The results obtained showed that NPN can be used as internal standard for calibrating PAN by using 1.3 as relative response factor. No problems were found in the shipment of PAN standard solutions so that the methodology used by the group can be extended to the EMEP monitoring network.

PAN and PPN determinations were carried out in the Tiber Valley upwind (Castel Porziano) and downwind (Montelibretti) the city of Rome. The results obtained showed that recirculation of polluted air masses might lead to substantial levels of PAN in locations placed upwind the city of Rome.

Values much lower than those recorded in 1992 were measured in Montelibretti. The drastic drop in the PAN and PPN levels was determined by changes in the meteorological conditions occurring in the Tiber Valley (lower radiation intensity) and the control measurements adopted by the local administration to reduce ozone and PAN levels in the city of Rome.

Participant no 8

CNSA

PAN STANDARD CALIBRATION (3rd Report)

By: Fernández Patier, R.; Bomboí Mingarro, M.T. and Herce Garraleta, M.D.

DETERMINATION OF PAN CONCENTRATIONS

The determination of NO_2^- by ion chromatography after the conversion of PAN to NO_2^- of alkaline hydrolysis is the used method for the analysis of PAN standard, which were sent by NILU.

Nitrite standard concentrations were prepared by dilution of 1 g. of NaNO_2 in a liter of Mili Q-Water. Then, four dilutions of 1.2, 2.6, 3.9, and 5.3 $\mu\text{g NO}_2^-/\text{ml}$. were prepared.

To perform the PAN hydrolysis, 200 μl . PAN standard to a tube containing 1 ml. of 0.025M NaOH was added and it was capped and shaken. After 15 minutes, 4 ml. of deionized water was added to each tube.

ANALYSIS OF NITRITE BY ION CHROMATOGRAPHY

The chromatograph utilised is a Dionex 2010i.

| | |
|--------------|--|
| Precolumn: | Dionex HPIC-AG4 |
| Column: | Dionex HPIC-AS4 |
| Suppressor: | Dionex anion type AFS-1 |
| Sample Loop: | 1.80 mM Na_2CO_3 /1.70 mM NaHCO_3 |

PAN ANALYZER

Many technical problems have been taking place since November 1992.

Firstly, the sampling pump was broken and after its reparation, the sensibility of the chromatograph was much lower. So, the data set obtained from January to April of 1993 was rejected. During May and June 1993, the PAN analyzer was carried to Castel Porziano (Rome) for the BEMA project. There we was able to calibrate and compare the results with the PAN analyzer of Dr. Ciccioni.

Although, the results of both analyzer showed a good relationship, we confirmed the lack of sensibility in our instrument.

Secondly, after the sampling campaign in our laboratory, more troubles happened. The main was the raise of frequency with time, at current constant.

Finally, we send the analyzer to Carlo-Erba. There, they found a high contamination of the carrier pipe line due to the use of a bad nitrogen cilinder.

Therefore, it was impossible to performe the calibration of PAN analyzer using the standard liquid solutions, now.

Un-official participant

JRC Ispra

JOINT RESEARCH CENTER
ENVIRONMENT INSTITUTE ISPRA

Y.LIBERT and H.GEISS

STEP-PAN intercalibration project
Progress report n°3
May. 93 - Dec. 93

I Analysis of the distributed standards of PAN :

The analytical technique was the same as that described in progress report n°1 as regards the procedure but this time we used an autosampler to make dilution, hydrolysis and introduction of sample.

Results are summarized in the following table :

| PAN STANDARDS ANALYSIS BY IONIC CHROMATOGRAPHY: ISPRA | | | | | | |
|---|-------|------------------------|--------|--------|--|-------------------------------------|
| REF/ DATE | | PAN by AC ⁻ | Hexane | Result | | PAN by NO ₂ ⁻ |
| A1 | 15.07 | 104,96 | 2,82 | 102,14 | | 98,84 |
| A1 | 9.08 | | | | | 98,23 |
| A1 | 8.11 | 97,1 | 2,82 | 94,28 | | 79 |
| B1 | 15.07 | 109,57 | 2,82 | 106,75 | | 103,1 |
| B1 | 9.08 | | | | | 99,4 |
| B1 | 9.11 | 104,25 | 2,82 | 101,43 | | 84,83 |
| C1 | 15.07 | 13,16 | 2,82 | 10,34 | | 10,97 |
| C1 | 9.08 | | | | | 10,68 |
| C1 | 9.11 | 13,15 | 2,82 | 10,33 | | 7,9 |
| D1 | 15.07 | 13,71 | 2,82 | 10,89 | | 11,13 |
| D1 | 9.08 | | | | | 10,59 |
| D1 | 9.11 | 13,05 | 2,82 | 10,23 | | 8,2 |

As we can see, the agreement between analysis of PAN made by I.C. for AC⁻ or NO₂⁻ in July and August were good within 5 to 6% .In November the agreement is only true within 20 to 25% and this without noticeable formation of NO₃⁻ .We must underline that, here at Ispra, stockage of PAN standards were made at a temperature in the order of -15°C which can allow some decomposition of the PAN. Nevertheless we can assume that this time there was no contamination of the standards by AC⁻ at the beginning.

II - Ambient PAN measurements

Starting in mid May 92 in the frame of this intercalibration activity, continuous measurements of PAN goes on at Ispra. We summarize the results using cumulated frequency of PAN at various level for the available measurements of each year. Figure 1 gives the percentuale of measured values of PAN, for each period, which are greater or equal to a certain level. It appears clearly that the level of PAN for 1993 is lower than that of 1992, this seems due mainly to the relative local levels of precipitation and of solar irradiation.

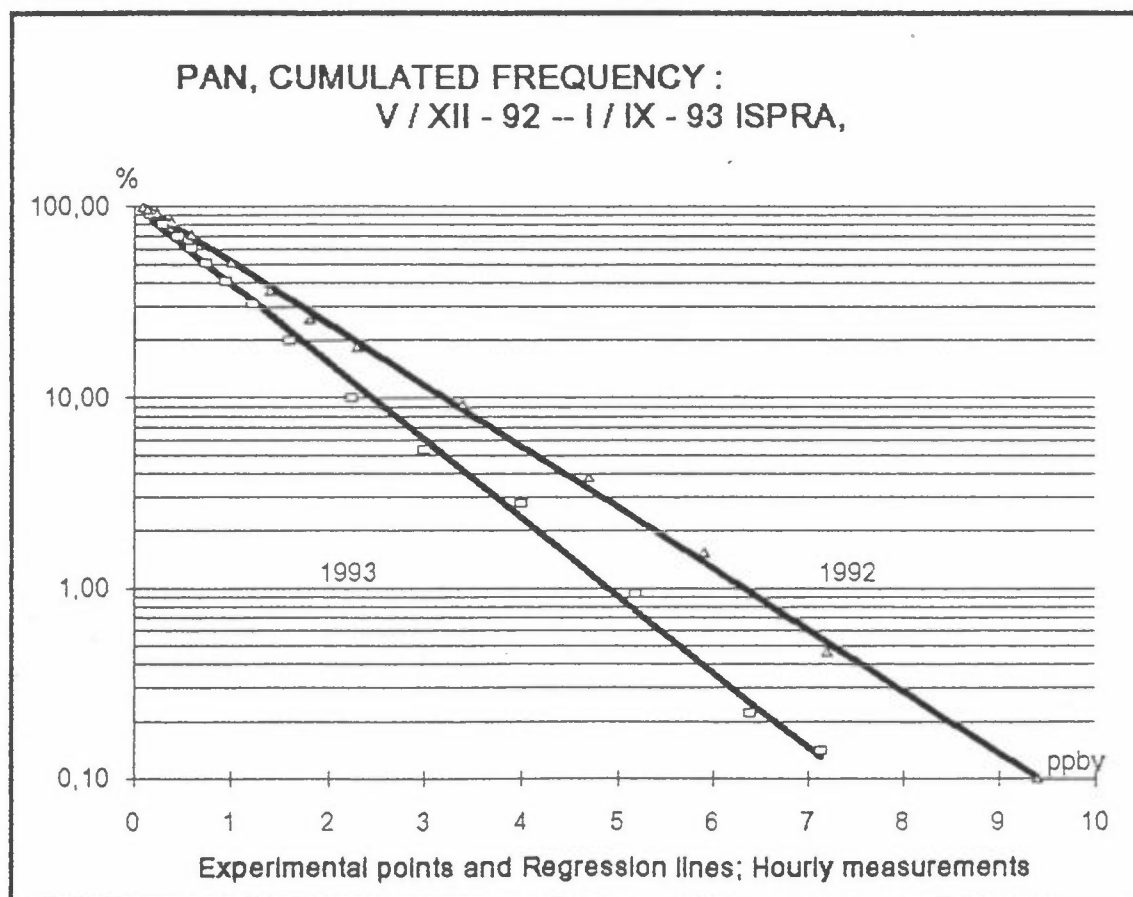


Fig.1

