

NILU : TR 7/93

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**Contract EV4V-CT90-
0222**

**Peroxy Acetyl Nitrate
Intercalibration**

**Progress Report no 2
1 May 1992 to 30 April 1993**

**Co-ordinator:
Terje Krognnes**



NILU

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



CONTRACT EV4V-CT90-0222
PEROXY ACETYL NITRATE INTERCALIBRATION
PROGRESS REPORT no 2
1/5-92 TO 30/4-93

CO-ORDINATOR:

T. KROGNES

NILU, July 1993

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 AEA Harwell participated in the first project year, but has not been active in the second year.

The delays reported from the last part of the first project year, have developed considerably, and a prolongation has been granted until the end of 1993. The delays are caused by continued technical problems with the main chemical analysis methods employed.

PREP.III

The last experiments (recalibration of returned standards) were performed at NILU in the early summer of 1992. The scientific report was distributed to the participants in a preliminary form in September 1992. The final report was still not finished at the end of the period.

Vennligst adresser post til NILU, ikke til enkeltpersoner/Please reply to the institute.

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CAL.I

Project phase CAL.I experiments have been performed, with results and accuracy similar to the findings of the trial distribution. The distribution took place in June 1992, and the standards were returned to the co-ordinator in December-January. In the trial distribution difficulties had been experienced with the use of the distributed pure hexane as matrix for IR measurements. This problem was solved before the CAL.I distribution.

During the trial distribution several participants had reported acetate contamination in the standards. This must have been caused by initial problems with some analysis methods. During the CAL.I experiments similar contamination problems were again reported, and this time turned out to be real. A defect HPLC pump caused contamination of acetic acid in the purified PAN standard. The acetic acid is needed to activate the column for the preparative separation of PAN from several contaminants. The acid is normally flushed out completely before the purification takes place. However, some parts of the system were not flushed due to a defect pump head.

Under normal conditions the contamination should have been detected before distribution of the standards. However, the IC calibration method was not usable at the time. This is the single technical problem that has caused the main part of all delays during the project. The analysis of acetate by ion chromatography was presented as the reference method of the intercalibration. Several participants reported difficulties with repeating the method that was initially used by NILU. And indeed, also at NILU the method has become unstable. It may work without problems for several years. Then unknown contamination sources may suddenly cause interference and baseline instability. During one period, a high blank value made acetate measurements inaccurate, and nitrite measurements were destroyed by large ghost peaks. The techniques for avoiding such errors in ion chromatography should be well-known. However, it is possible that the solvent residues that are dissolved in the water samples during PAN hydrolysis may cause new problems that are not so well known. The complete report of CAL.I will be ready in September 1993.

STRATEGY MEETING IN ROME

A meeting of the participants of the project was arranged in Rome on 27 and 28 October 1992. Administrative and technical details of the project were discussed.

FURTHER WORK

The next standard distribution (CAL.II) will be started in June 1993. The last standard distribution (CAL.III) will be performed before the end of 1993. A prolongation of the project has been granted until the end of 1993. The schedule for the rest of the year will be very tight.

Participant no 1

Norwegian Institute for Air Research

PARTICIPANT NO 1, NILU

WORK PERFORMED AND RESULTS OBTAINED

The final experiments of the project phase PREP.III were performed at NILU in the spring of 1992. The scientific report was distributed in a preliminary version. Important material from one participant is still not arrived at NILU.

The standards for project phase CAL.I were purified, calibrated and distributed. After experiments in the laboratories of the participants, samples of the standards were returned to NILU. These were scheduled for re-calibration in the spring of 1993.

During the summer of 1992 the method for ion chromatographic analysis of acetate could not be repeated at NILU in the manner described before. Extensive work was performed to locate the source of contamination or other error sources. The original method has now been taken out of active use, as it is not sufficiently robust. A new analysis method based on the new AS11 column, with NaOH eluent (concentration gradient) is now employed, and allows analysis of both acetate, nitrite and nitrate in a single run. There are ambiguities in the interpretation of a PAN calibration based on nitrite, as nitrite may react and form nitrate before the analysis is complete (multiple pathways with different stoichiometry have been suggested). This must now be considered a minor problem compared to the error sources encountered in acetate analysis.

FURTHER WORK

NILU will continue participation in the project according to the revised work schedule submitted with the prolongation application in May 1993. Further adjustments to reduce the time span will be employed where possible.

Participant no 2

University of Paris XII

UNIVERSITE PARIS XII- CRETEIL (FRANCE)

P. COLIN and G. TOUPANCE

EEC STEP-PAN intercalibration project.

Progress report n°2
May 1992-May 1993

I - Analytical technique :

1 - IC of NO₂⁻ and AcO⁻ ions

We have changed a part of the analytical technique. Now, after hydrolysis the volume is filled up to 10 ml by mili-Q water and the flow rate of eluent is 2ml/mn. The analytical procedure is the same as reported in progress report n°1.

2 - Saltzman technique

Exactly the same technique reported in progress report n°1.

3 - Modification in preparation of solutions for injection into the GC-ECD:

The aliquot of PAN (prepared by the classical technique of nitration of peracetic acid) is diluted by hexane to 1/200.000 for calibration of analytical technique and to 1/400.000 for calibration on field measurements at PORSPODER in Bretagne.

0,1µl to 1µl of these solutions are injected into the GC-ECD and the response is plotted as a function of sample volume.

II - Trial run :

Due to the late receiving of the samples just before the summer 1992 vacation period, the whole set of analysis was not finished before the break for holiday. Unfortunately, important works done in the buildings during the break have resulted in a prolonged electric power failure. A strong alteration of the samples was observed when returning. So only the preliminary results obtained before the summer break are reported here.

1 - Analysis by Saltzman technique

1.1- Experimental :

Solutions 100 µg/ml and 10 µg/ml : Operation is the same as described in progress report n°1. Each experiment is repeated 3 times and the mean value is calculated.

1.2 - Results

Solution PAN 100 µg/ml :	98,48 µg/ml
Id + NPN 100 µg/ml :	Not tested
Solution PAN 10 µg/ml :	12,18 µg/ml
Id + NPN 10 µg/ml :	Not tested
NPN 100 µg/ml :	Not tested

2 - Analysis by IC

2.1 - Experimental :

Operation is the same as described in progress report n°1. Unfortunately, the experiment were realised only once due to destruction of samples during summer (see above). Analysis of acetates was impossible due to temporary troubles both on pump column.

2.2 - Results for NO₂⁻

Solution PAN 100 µg/ml :	98,20 µg/ml
Id + NPN 100 µg/ml :	Not tested
Solution PAN 10 µg/ml :	12,42 µg/ml
Id + NPN 10 µg/ml :	Not tested
NPN 100 µg/ml :	Not tested

III - Modification of the equipment :

Our HPLC system have been equiped with a new Vydac 302IC column for acetate, nitrite and nitrate analysis since December 1992.

IV - Field measurements :

The TOR station of PORSPODER (Bretagne, France) gives continuous data for PAN, as well as for O₃, NO, NO₂ and individual hydrocarbons. It is operated since march 1992. 4 days backtrajectories are routinely provided for 0H and 12H UT, which allows a detailed classification of the data by origins of air masses. The most discriminant classification is trajectories purely marine in the past 4 days versus all others.

Until november 1992, the detection limit of our PAN analyser was 40 pptv of PAN. The whole set of data obtained from March to november 1992 shows that the concentration of PAN in marine air is always below the detection limit during this period, that is always <40 pptv. Since december 1992, the detection limit has been lowered down to 10 pptv in routine measurements. Detailed analysis of the variation of PAN in marine air is now possible.

On the contrary, our results show that concentrations of some hundreds pptv are typical of any other air masses which have a part of their history on land. Subdivisions within this series of "continental" air masses has been done, from spain to continental, scandinavian and british iles origins, and the discussion of this more accurate set of data is under progress.

V - - Continuation :

As planned in the general lines of the program.

Participant no 3

University of Patras

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

Contractor : University of Patras
Department of Chemistry

Leading Scientist : Dr. Sotirios Glavas

Scientific Staff : Demetrios Danalatos

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I. OBJECTIVES FOR THE REPORTING PERIOD:

To improve the analytical methods for the determination of PAN by IC.

To analyze using both acetate and nitrite analysis of the distributed by NILU PAN standards of phase CAL I.

To collect and evaluate the ambient PAN measurements at the University of Patras.

II. OBJECTIVES FOR THE NEXT PERIOD:

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

To correlate the automatically collected ambient PAN concentrations with ozone measurements and meteorological data.

III. MAIN RESULTS.

PAN INTERCALIBRATION.

Our results of the first trial distribution of PAN standards indicated that our IC nitrite measurements compared to the IC acetate ones were significantly low. We found that in order to improve our nitrite method of analysis we had to improve the resolution of the nitrite peak from the system peak when we use as eluant $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ in our AS4A column. We also found that the system peak is due to the alkalinity of the sample and is not affected by the presence of the solvent hexane. For this purpose we treated our samples with the On-Guard H 39596 filters made by Dionex. These filters turned out to improve the resolution of the

nitrite peak but at the same time they affected the peak height of the nitrite peak. The calibration has thus become more elaborate but despite this difficulty this method is considered better than without the use of the Dionex filters.

The additional method for the analysis of the nitrites and which we now prefer, is the use of borax as eluant. This eluant allows us to determine simultaneously both the nitrites and the acetates. In Table 1 below we list the results of the first intercalibration. We report our results of the PAN concentration determined with both eluants $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ for nitrites and borax for nitrites and acetates.

Table 1

Results of analyses of first PAN intercalibration, μg PAN/ml hexane.

Standard	Acetates Borax as eluant	Nitrites	Nitrites $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ eluant
A-4	56.4($1\sigma=8.9$)	59.4($1\sigma=6.7$)	60.0($1\sigma=4.3$)
B-4	43.7($1\sigma=2.2$)	58.1($1\sigma=4.6$)	44.0($1\sigma=6.4$)* 50.9($1\sigma=8.3$)*
C-4	18.8($\sigma=1.3$)	8.1($\sigma=1.6$)	6.8($\sigma=0.9$)
D-4	32.8($\sigma=2.3$)	-	6.0($\sigma=1.3$)
NILU'S hexane	12.3	-	0

* same sample analyzed on two different time periods.

As we can see from above Table the results of samples A-4 and B-4 using all methods of analyses are in agreement. However the results of C-4 and D-4 indicate a lot higher acetate concentration than nitrite. This prompted us to analyze also the hexane solvent provided with the standards by NILU: We found that hexane contained the equivalent of 12.3 $\mu\text{gPAN/ml}$ and zero nitrites. We further analyzed the hexane solvent by ECD and we found that it was also contaminated by NPN! We hydrolyzed NPN in alkaline solution and we found that it is hydrolyzed by 5% yielding nitrite anions.

We now know that NILU had a contamination problem with acetates.

AMBIENT PAN MEASUREMENTS AT THE UNIVERSITY OF PATRAS

Since March 1992 we are operating an automatic PAN analyzer at the University campus. In addition from our own funding we

purchased and operate an automatic ozone analyzer. In Table 2 below we list the mean monthly values for 1992 of PAN as well as its maximum monthly value and the corresponding ozone concentration.

Table 2

Ambient PAN and Ozone concentrations at the University of Patras.

Month	Mean monthly value, ppb	Maximum monthly value, ppb	Ozone, ppb
March	1.09	1.8	-
April	1.00	2.0	-
May	0.64	1.3	61.2
June	0.51	1.6	53.9
July	0.92	2.3	71.8
August	0.91	2.2	93.5
September	1.08	1.9	65.6
October	1.07	2.4	-
November	0.90	1.8	-
December	0.57	1.5	35.8

Participant no 4

TNO

Annex to letter - 931789.

Progress report STEP PL 900289 "PAN INTERCOMPARISON".

J.C.Th. Hollander, TNO-Institute of Environmental Sciences
P.O. Box 6011, 2600 JA DELFT, The Netherlands.

Following the trial intercomparison (PREP III), the first (CAL I) of the planned three intercomparisons was carried out.

As in the trial intercomparison, PAN standard solutions distributed by the coordinator and solutions synthesized in our laboratory were analyzed by FTIR and ionchromatography of acetate and nitrite after hydrolyses. Nitrate analyses were omitted because only a small fraction of PAN hydrolyses to nitrate (nitrite being the main product), which does not allow an accurate analysis.

Analyses were carried out shortly after arrival of the samples from the coordinator and repeated shortly before returning them to the coordinator. Gas chromatographic analyses in between had to be omitted this time because of an ill-fated journey to the monitoring site and in addition finding the PAN analyzer not in proper operation after final arrival.

Since the acetate analysis by ion exclusion chromatography did not perform satisfactorily at low concentrations during PREP III and even over larger concentrations ranges during first analyses of CAL I, the method was replaced by ion exchange chromatography which proved more reliable and gave a lower limit of detection. The detection limit for nitrite could also be improved slightly.

As in the trial intercomparison, again systematic differences were observed between the IR-spectra of PAN standards of different origin, although of different nature.

Due to the improved performance of the acetate analysis and by extensive analysis of blanks and solvents used in the preparation of the samples it could be concluded that acetate impurities were present in the samples distributed by the coordinator for CAL I.

It has to be admitted that the IR-absorptioncoefficients for PAN in solution have not been established firm by so far, giving rise to possible systematic errors in PAN concentrations derived by FTIR. On the other hand IR-spectra are a powerful tool to establish the quality of PAN standards.

The results of the trial intercomparison and preliminary results of CAL I were discussed during a two day meeting in Rome hosted by Dr. P. Ciccioli.

Ambient PAN-measurements, which started in July 1991, were continued at the monitoring site Kollumerwaard up to the moment of writing this progress report. This will ensure sufficient overlap with monitoring periods by other participants at different locations.

All 1992 data were corrected by reviewing the calibration data over the measurement period. A graphical summary of the data for distribution to the participants has been prepared.

Delft, June 1993.



Participant no 5

Meteorologie consult gmbh

Status-Report of the EG-STEP-PAN-PROJECT for 1992/1993

Dr. Rainer Schmitt

**Meteorologie Consult GmbH
D-6246 Glashütten**

During the period 1992/1993 of the project the PAN-liquid standards which has been distributed by NILU has been analyzed with success using ionchromatographic. Both acetate and nitrate were analyzed successfully. In addition our gasphase PAN-standard (photosynthesis of PAN from NO₂ and/or from NO has been calibrated against the liquid PAN standard. According to our analysis of the liquid standard the gasphase PAN showed - as evaluated before- a constant 85% conversion form NO/NO₂ to PAN. For this comparison the liquid PAN-standard was injected into the gasphase reaction vessel.

In addition to this calibration a number of test with a dynamic gasphase PAN-production were performed in order to achieve a reliable PAN-standard for mobile use.

Our continuous measurements at the Baseline station IZANA Tenerife did continue without mayor disturbances. Fully automatic PAN measurements are performed every hour. The detection limit is as low as 0.05 ppt using a low-temperature pre-concentration step.

PA1006-1

Report STEP PAN INTERCALIBRATION

(May 1992 to May 1993)

J. Rudolph (principal investigator), K. P. Müller, W. Schrimpf

**Institut für Atmosphärische Chemie Jülich, Forschungszentrum Jülich,
52425 Jülich, Germany**

The activities in 1992/1993 centered on 3 tasks:

- Test of different calibration methods
- Analysis of the samples from the first PAN intercalibration round (CAL 1).
- Modification of PAN measuring techniques to improve stability and reproducibility

The calibration tests were based on the comparison of 3 different methods: injection of PAN in solutions, injection of PAN in nitrogen from a permeation system, and photolytic generation of PAN from NO₂ and acetone in the gas phase. Calibration of the PAN solution and the PAN permeation system is done by hydrolysis in alkaline solution and subsequent nitrite measurement (see previous method description). The photolytic calibration is based on the known NO₂ concentration and a nearly quantitative yield (about 90%) of PAN with respect to NO₂. The reproducibility of the measurements is about 4% for liquid sample injections with a syringe and 1.5% for gas injections with a gas sampling valve. Different calibrations are consistent and reproducible within better than 5%. For photolytic PAN calibration the comparisons are based on a 90% PAN yield.

The results of the CAL 1 intercalibration round have already been reported. In summary, the four CAL1 PAN solutions were analyzed by two different methods:

- Hydrolysis in alkaline solution and subsequent nitrite measurement (see previous method description).
- Gaschromatographic analysis by comparison with PAN solutions of known PAN concentrations.

The relative variations within one method were about 1%, the differences between the two methods always less than 3%. A comparison with photolytically produced PAN gave results which were consistent with a 90% yield for photolytic PAN generation within 5%.

The PAN measuring developments focussed on 3 points:

- improve the lower limit of detection
- eliminate the "conditioning problem"
- improve separation and reduce analysis time

In summary the following changes were made:

- Use of a megabore capillary column for separation.
- Moisturizing of the carrier gas and make up gas.
- Reduction of make up gas flow rate.

The resulting improvements were:

- Lower limit of detection of 10^{-13} g PAN.
- Time for separation less than 5 min with very good resolution.
- No conditioning necessary for stable signal.
- Reproducibility better than 1%.

Participant no 6

ARD (name now changed to ITM)

STEP PAN INTERCALIBRATION

CONTRACT EV 4V-CT90-0222

PROGRESS REPORT NR 2

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 May 1992 and April 1993.

1.- Test of a PAN-analyzer dynamic calibration method.

The use of an alternative dynamic system to calibrate the PAN-analyzer, based on the use of a glass calibrator has been tested. This calibrator filled with a liquid PAN-standard is submerged in a cryo-bath at a programmed temperature, where liquid PAN is diffused through a very thin glass tube (1,5 mm I.D.) mounted inside the same glass calibrator, reaching the PAN-analyzer and allowing a dynamic calibration of the instrument.

The results of the PAN-instrument have also been checked by parallel injections of PAN-standard into a Chemiluminescence NO-Analyzer (Eco-Physics al-ppt) previously connected to a NO₂ --> NO-converter (Master Blaster). The whole procedure will be separately described in greater details.

2.- Continuous sampling. An intensive all Nordic measurement campaign.

According to a all Nordic countries intensive measurement campaign, since 15th February 1993, the PAN-analyzer has been working for unattended routine measurement of background levels of PAN at our station - Aspvreten. This measurement campaign will be concluded by the end of June 1993.

3.- Intercalibration Programme.

According the schedule of the STEP PAN Intercalibration project (and the co-ordinator) the APL have already participated at the first phase of an intercalibration programme - The Trial Pan Standard Distribution. The start of the second phase of this programme has been already scheduled to the coming next weeks.

4.- Visit of the co-ordinator of the STEP-PAN project to APL, Studsvik, Sweden.

The visit of the co-ordinator of the STEP-PAN project Mr Terje Krognnes to the Air Pollution Laboratory (APL) of the Institute of Applied Environmental Research at the Stockholm University (the former Swedish Environmental Protection Agency, Air Pollution Division) took place on 27 and 28 August 1992.

During the visit of the co-ordinator, a new Electron Capture Detector (ECD) controller module has been mounted in the PAN-analyzer. The new ECD controller was set to operate in constant frequency with 20 V pulse height, 3- μ s pulse width and 900 Hz frequency.

The new electronic module with a built-in facility for baseline corrections, give substantial improvement in terms of PAN peak size and shape.

Participant no 7

CNR

REPORT ON THE ACTIVITY CARRIED OUT BY THE I.I.A.-C.N.R. DURING
THE SECOND YEAR OF THE PAN INTERCALIBRATION PROJECT.

P. CICCIOLO

Istituto sull'Inquinamento Atmosferico del C.N.R. - Area della
Ricerca di Roma, Via Salaria km 29.300, C.P. 10, 00016
Monterotondo Scalo- ITALY.

The activity of the second year of the PAN Intercalibration Program was devoted to:

- a) determine the content of PAN in the solutions provided by the co-ordinator.
- b) calculate the response factor of PAN relatively to n-propyl nitrate (NPN) to circumvent the difficulties associated with the preparation and quantitation of PAN standard solutions for the calibration of GC-ECD based PAN monitors.
- c) monitor the levels of PAN in the Tiber valley and various sites of Italy.

The content of PAN in the standard solutions provided by the co-ordinator were determined by ion liquid chromatography after alkaline hydrolysis and GC-ECD. GC-MS was used to evaluate possible interfering compounds possibly present in the solutions. The amount of PAN in the alkaline solutions was evaluated through the measure of the nitrite ion that resulted quite specific and not affected by other impurities coming from the synthesis. By combining these three techniques the content of PAN and PPN in the solutions were accurately quantified. A relative response factor of PAN with respect to NPN equal to 1.3 was determined. This made possible a quick calibration of the GC-ECD PAN analyzer under the monitoring conditions experienced in field campaigns. The response of PAN was checked every week for three months and resulted to be constant for long time.

PAN and PPN were continuously monitored in the Tiber Valley (Montelibretti and Castel Porziano) and for short periods in the city of Milan. Levels of PAN (52 ppbv) much higher than those measured in the most polluted areas in the world were recorded in the station located downwind the city of Rome (Montelibretti) during some photochemical smog episodes occurring in the summer of 1992. High levels were also measured in the station placed upwind (Castel Porziano) with values as high as 6-7 ppbv. Such high levels in a forest area located near the sea shore were attributed to the recirculation of polluted air masses caused by the sea-, land-breeze system dominating the movement of the air masses in the Tiber Valley. The values recorded in Milan were quite low being the photochemical reactivity of the atmosphere rather limited during the time were monitoring was carried out.

Participant no 8

CNSA



MINISTERIO DE SANIDAD Y CONSUMO

INSTITUTO DE SALUD CARLOS III

SUBDIRECCION GENERAL DE CONTROL

Summary of activities in the PAN intercalibration project
Centro Nacional de Sanidad Ambiental

From 1 May 1992 to 31 April 1993, the C.N.S.A. has carried out an exercise of intercalibration of PAN standards prepared by NILU.

In addition, field measurements of PAN have been made in two sampling points in Madrid: Majadahonda and Loeches. The last sampling point also participates in a national project of "formation, transport and deposition of photochemical smog in Madrid", in which four ten-day campaigns were carried out during the year. In the Spring campaign a good relationship between the level of ozone and PAN was obtained, but during the summer campaign, existed some problems due to the temperature of the room and no stabilization of the apparatus.

In following campaigns concentrations of PAN were not detected due either to the no existence of PAN in the ambient air or for adsorption of this pollutant by the sampling line. This last hypothesis is being tested in the laboratory.

