

NILU : OR 23/94

NILU : OR 23/94  
REFERENCE : U-91051  
DATE : JUNE 1994  
ISBN : 82-425-0568-3

**Peroxy acetyl nitrate  
intercalibration  
Final report  
STEP EV4V-CT90-0222**

**Co-ordinator: T. Krognes**

---

NILU : OR 23/94  
REFERENCE : U-91051  
DATE : MARCH 1994  
ISBN : 82-425-0568-3

**Peroxy acetyl nitrate  
intercalibration  
Final report  
STEP EV4V-CT90-0222**

**Co-ordinator: T. Krognnes**

**Authors:**

**Toupance, G., Univ. Paris XII, France  
Glavas, S., University of Patras, Greece  
Hollander, C., Th., TNO, The Netherlands  
Schmitt, R., Meteorologieconsult, Germany  
Oyola, P., APL, Sweden  
Ciccioli, P., CNR, Italy  
Patier, R.F., CNSA, Spain  
Rudolph, J., KFA Jülich, Germany  
Libert, Y., J.R.C. Ispra, Italy  
Krognnes, T., NILU, Norway**

---

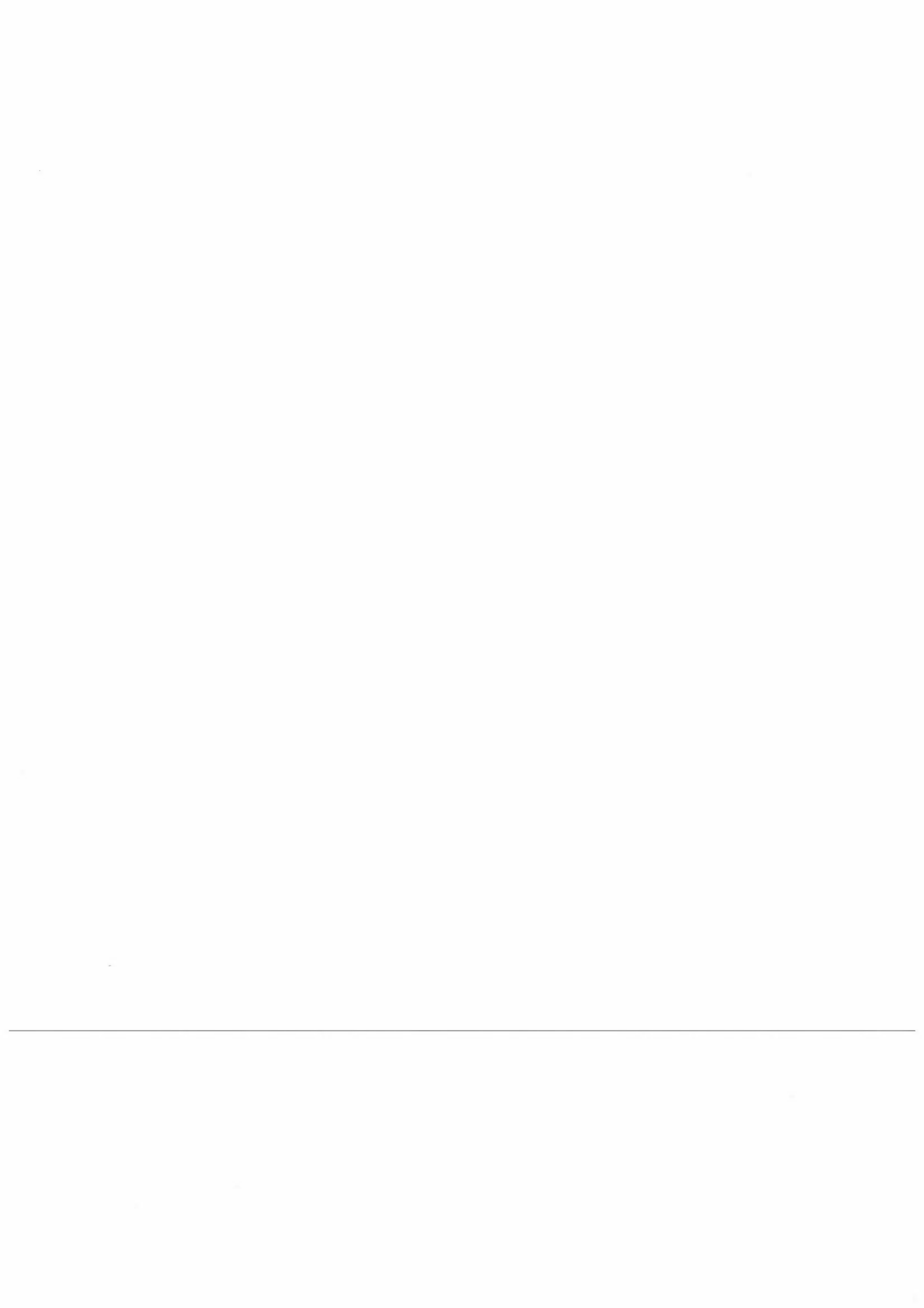
## Preface

This is the final administrative report to the CEC of the work under the contract STEP EV4V-CT90-0222. The project is named "Peroxy acetyl nitrate intercalibration". The project was formally ended 31 December 1993. However, the work has been delayed due to technical difficulties with the analysis methods involved. These delays have also caused delays in interpretation and reporting of the results.

A draft version was presented at the end of March 1994 and was discussed by the participants in a project meeting 27-28 April. Contributions have been enclosed from J.R.C. Ispra and from KFA Jülich, and both have contributed actively in the research as informal project participants. Also the AEA Harwell has received PAN solutions and will contribute with ambient monitoring results, but no enclosure is available for this administrative report.

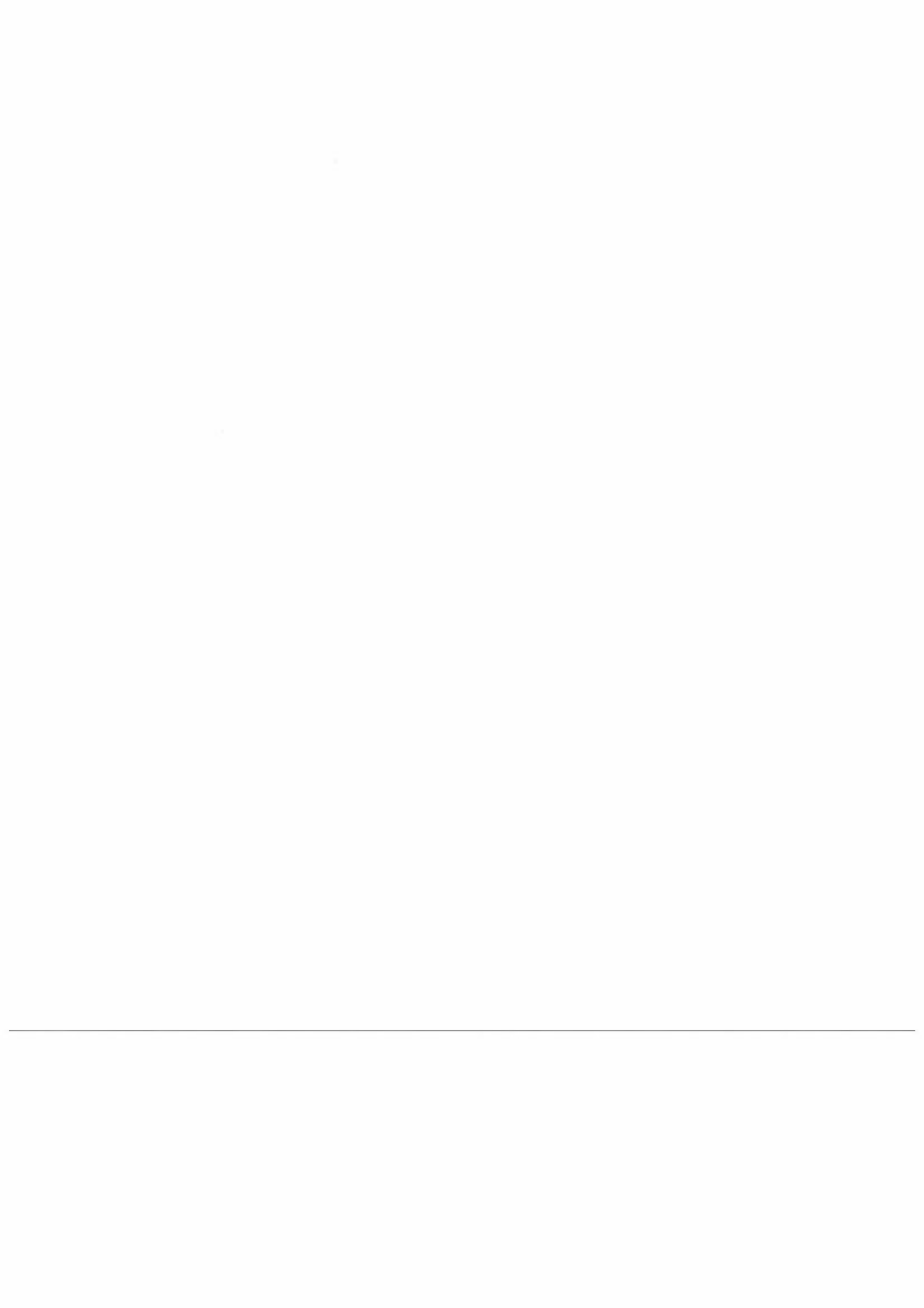
The co-ordinator will express thanks to Dr. Angeletti in the CEC, for support in the planning of this final report. Furthermore, the co-ordinator will express thanks to the participants for good co-operation in a technically complex project.

---



# Contents

	Page
<b>Preface .....</b>	<b>1</b>
<b>1. Introduction .....</b>	<b>5</b>
<b>2. Main objectives and corresponding results.....</b>	<b>5</b>
2.1. Calibration of a PAN solution.....	6
2.2. Calibration of a PAN GC.....	7
2.3. A European platform for comparison of PAN data .....	8
2.4. Ambient PAN monitoring.....	8
2.5. Publishing of results.....	8
<b>3. Dissemination of results .....</b>	<b>9</b>
<b>4. Conclusions .....</b>	<b>10</b>
<b>Appendix 1: NILU (Co-ordinator) .....</b>	<b>13</b>
<b>Appendix 2: University of Paris XII.....</b>	<b>17</b>
<b>Appendix 3: University of Patras .....</b>	<b>23</b>
<b>Appendix 4: TNO.....</b>	<b>35</b>
<b>Appendix 5: Meteorologieconsult gmbh .....</b>	<b>39</b>
<b>Appendix 6: CNR.....</b>	<b>43</b>
<b>Appendix 7: CNSA.....</b>	<b>51</b>
<b>Appendix 8: APL (subcontractor under NILU).....</b>	<b>55</b>
<b>Appendix 9: KFA Jülich (independent participant co-operating with     Meteorologieconsult.....</b>	<b>59</b>
<b>Appendix 10: J.R.C. Ispra (independent participant .....</b>	<b>63</b>
<b>Appendix 11: AEA Harwell (independent participant) .....</b>	<b>67</b>



# Peroxy acetyl nitrate intercalibration. Final report

## STEP EV4V-CT90-0222

### 1. Introduction

PAN (peroxy acetyl nitrate) is a highly reactive and thermally unstable photo oxidant. It is formed in the atmosphere when a mixture of nitrogen oxides and organic compounds is irradiated by sunlight. It is an important reservoir for nitrogen oxides in the atmosphere. PAN interferes with many types of  $\text{NO}_x$  monitors. In large cities and industrial areas PAN is an important component of photochemical "smog". It may cause irritation of respiratory organs, and in some cases cause plant damage.

One country (Italy) presently has passed legislation that includes PAN among the air quality parameters that shall be monitored in polluted areas. Good monitoring and calibration methods are required to fulfil the purpose of such legislation. The emission of nitrogen oxides ( $\text{NO}_x$ ) is subject to international treaties. To control the effect of such treaties, monitoring and modelling of  $\text{NO}_x$  components is required. PAN is not the major component, but a significant part of this picture in central European areas. In arctic areas, PAN is a major component of  $\text{NO}_y$ , and a large contributor to  $\text{NO}_x$ .

Since PAN is thermally unstable, certified PAN standards cannot be made. A laboratory preparing to calibrate a PAN monitor, will in most cases purchase or synthesize a solution of PAN in hexane (or another suitable solvent). The solution normally needs to be purified by HPLC (high performance liquid chromatography) and diluted to a suitable concentration. The next step is to calibrate the diluted PAN solution. A much used method is IC (ion chromatography) after alkaline hydrolysis of the PAN solution. The calibrated PAN solution may at last be used to prepare a dilution of PAN in clean air. The PAN monitor is calibrated by sampling the dilution that has a known concentration of PAN.

The elements included in the calibration of a PAN monitor are complex, and the error sources numerous. The lack of certified standards leaves the individual laboratory more or less alone with this complicated set of procedures. An international intercalibration project was required to break this isolation and compare methods and results.

---

### 2. Main objectives and corresponding results

The main objectives defined in the Work Programme are recalled and the results briefly presented and commented in the following sections.

## 2.1. Calibration of a PAN solution

The primary goal of the project was *to enable the participants to calibrate a PAN solution with errors within  $\pm 10\%$  of the true concentration.*

There were four major problem areas:

- The comparison of PAN solution calibration methods depended on our ability to transport PAN solutions between laboratories in different countries without significant loss of PAN. Due to the reactivity and thermal instability of PAN, the solutions must be transported by air, packed with dry ice. The dangerous goods formalities and customs handling routines provide formidable problems.
- At the beginning of the project it was not known if the differences between available methods would be in the  $\pm 20\%$  range or in the  $-50\%$  to  $+200\%$  range, since most laboratories only used one or two methods.
- When the same method was repeated in different laboratories, the uncertainty could be even larger, since many error sources are connected to minute details. Such details are often part of the general procedures in a laboratory, and not recorded in method descriptions for publication.
- There is no "true" concentration of PAN in the solutions that our results can be compared to. There is no objective point of reference. Some "reference" must be extracted from a series of experiments where both systematic and random errors are unknown factors.

The transport problems were solved successfully. A styrofoam box with a cardboard outer box is made specially for transport of dry ice. This box was insulated internally with an extra 5 cm of styrofoam. The outer box fits perfectly in a plywood box that is certified for air transport of dangerous goods. The bottles were packed in a 1/3 litre tin can surrounded by approximately 12 kg of crushed dry ice. The parcel would keep the solutions safely frozen for approximately four days.

The customs formalities and dangerous goods formalities were worked out in minute detail to avoid delays during transport. As a result, only 3 of 50 transports suffered serious delays (one of those was lost in a warehouse, and appeared several months later). For the majority of the transports, no decay of the solutions can be attributed to the transport conditions.

Originally 4 distributions of PAN were planned. 3 distributions have been completed within the time frame of the project.

The "true" PAN concentrations were established as the averages of those results that were not ignored as outliers. This removes most random errors from the "true" reference, but systematic errors may still be included.

---

7 or 8 of the 10 participants are presently likely to calibrate a 100  $\mu\text{g}$  PAN / ml hexane solution with errors within 15% of this "true" reference. In this estimate, approximately 10% of the results (not systematically from the same laboratories) of the third distribution have been discarded as outliers. For the dilute solutions (10  $\mu\text{g}$  PAN / ml hexane) the corresponding error limits are approximately  $\pm 25\%$ .



The range of errors is somewhat larger than the goal of  $\pm 10\%$ , as foreseen in the Work Programme. The result is good, considering the complexity of the task. Furthermore, the measured error range includes both calibration errors and storage decay. These two are difficult to separate, since instruments and methods do not always function perfectly the month the experiments should be performed. The result is relevant as a measure of the accuracy of the PAN standards normally used for PAN monitors - also those standards are stored and used several months between calibration and re-calibration.

The most important gain of the project, is that the error sources have been illuminated. Even if many error sources have not been separately quantified, the quality of the PAN solution calibrations may now be based more on knowledge than on estimates.

The project has also revealed that a PAN solution should not be calibrated by acetate analysis alone. A solution that has been partially destroyed by overheating, may still yield the same amount of acetate in alkaline hydrolysis. The other compound formed in the hydrolysis of PAN is nitrite. Nitrite does not appear to be formed by the by-products of PAN decomposition. Nitrite analysis is therefore a better way to control the integrity of a PAN solution. In most cases before, acetate analysis has been avoided only due to the added complexity connected to analysis of weak organic acids.

## **2.2. Calibration of a PAN GC**

A goal of the project was to *enable the participants to calibrate a PAN GC with errors within  $\pm 10\%$  of the true sensitivity.*

In the original project proposition a field intercomparison of PAN GCs was suggested. This element was removed during the contract negotiation to keep the cost within acceptable limits. This also removed the possibility to compare among the participating laboratories the results of PAN GC calibrations. A mobile GC suitable for transportation to the participants was an optional item mentioned in the NILU work programme. NILU did not find it possible to realise this option within the time frame of the project.

The participants had identical, distributed PAN solutions at their disposal, and used those for calibrating their PAN GCs. The comparison with locally produced and calibrated standards was very good.

Different PAN monitors react differently to variations in the sample matrix. The sensitivity to PAN in a calibration experiment may not be the same as the sensitivity to PAN in an ambient air sample. Two small scale comparisons (supported only by the respective laboratories) have been performed by participants of the STEP project. The CNSA has visited CNR in Rome with their PAN instrument. NILU has taken part in a PAN instrument intercomparison in Offenbach with Meteorologieconsult and UBA (the Umwelt Bundesamt). The Offenbach effort demonstrated that different PAN monitors may react very differently to the same calibration standard. Hopefully, preliminary results from these local efforts may be made available in the technical report of the project.

The project group is considering the possibility of performing a field intercomparison of PAN monitors and GC calibration methods. This would be a natural next step after completion of the present project.

### **2.3. A European platform for comparison of PAN data**

A goal of the project was to *create a European platform for comparison of PAN data*.

Through the successful transport of PAN solutions and comparison of methods for calibration of the solutions, the first half of this task is accomplished. The European platform has been established for quality control of PAN solution calibration. To gain control of the ambient monitoring data quality, also a field intercomparison of the PAN monitors (GCs) and the GC calibration methods is needed (as suggested above).

### **2.4. Ambient PAN monitoring**

A goal of the project was to *provide a set of well-calibrated ambient PAN data from a European net-work of measurement stations*.

This goal has been reached in the respect that a set of data is available for approximately two years. The availability of data is good for most of the participants. However, the lack of a PAN monitor intercalibration (see the two previous sections) prevents us from quantifying the differences in GC calibration quality between the participants.

For a proper evaluation of the PAN concentrations over Europe, extensive knowledge of both local and regional circulation patterns and precursor sources is required. Complex modelling tools are required to relate the PAN observations to other observed and computed parameters. Since PAN is reactive and short-lived, the chemical processes in the atmosphere must be modelled in great detail, both in space and time. In this respect our PAN monitoring data set is very small.

To maximize the value of the work already performed, the group should cooperate with modellers, and put both present and future data sets at their disposal.

### **2.5. Publishing of results**

A goal of the project is to *publish results in reviewed journals*.

Presently such publications have not been written. The following internal reports have been produced during the project:

- 
- "STEP PAN intercalibration preparations, Project planning, Part 1" (NILU TR 7/90). This report is a collection of letters and documents including from the early preparation phase, including the project proposal.
  - "STEP PAN intercalibration preparations, Project planning, Part 2" (NILU TR 4/91). This report is a collection of letters of documents from the contract negotiation phase, including the project contract.

- "Phase PREP.I internal work document" (NILU TR 7/91). A collection of method descriptions previously published by the participants.
- "Description, Users Guide, Calibration and Test Results of an Analyzer for PAN in Ambient Air." (TNO-report R 91/156)
- "Phase PREP.II internal report" (NILU TR 11/91). In this report the participants have described refinements to existing methods, and procedures to be used during the intercalibration experiments.
- "Visit to Meteorologieconsult, KFA (Jülich) and TNO (Delft), April 1992" (NILU RR 8/92). Includes details of technical topics discussed during the visits.
- "Visit to ARD, Studsvik, Sweden" (NILU RR 16/92). Includes details of technical topics discussed during the visits.
- "Trial distribution of PAN standards". First draft of the technical report of the trial PAN distribution. November 1992.
- "PAN solution intercalibration, Technical report of first (trial) distribution, 2 draft" (NILU TR 8/94). Second draft of the above document, March 1994.
- "PAN solution intercalibration, Technical report of second distribution, 1 draft" (NILU TR 9/94). March 1994.
- "PAN solution intercalibration, Technical report of third distribution, 1 draft" (NILU TR 7/94). March 1994.

The above reports are mainly for internal use. The dissemination in publications is treated in a following section.

### 3. Dissemination of results

The Work Programme includes a short description of four planned publications. The main publication (the comparative study of PAN calibration methods) will be completed in the planned form. The three planned data monitoring reports will probably be compressed into one publication, and some of the monitoring data sets will be published separately.

Three technical reports (one for each of the three PAN solution distributions) contain a large amount of technical information. In these reports all results are directly related to the respective participants, and the reports are intended for internal use in the project group. The material is being compressed in two steps. The first of these steps will be a CEC report. Here, in part 1 the intercalibration results will be described. The calibration results will not be related directly to the respective participants. In addition to the conclusions, detailed recommendations will be included for other scientists that need to perform PAN solution calibration. Part two will be a collection of papers on PAN GC calibration and on ambient PAN monitoring results.

Part 1 of the CEC report will be further compressed and submitted to a reviewed journals for publication. This is the main publication of the project, as described above. The dissemination is illustrated in the figure below. The co-ordinator has requested information from the CEC regarding the formal requirements for producing a CEC report.

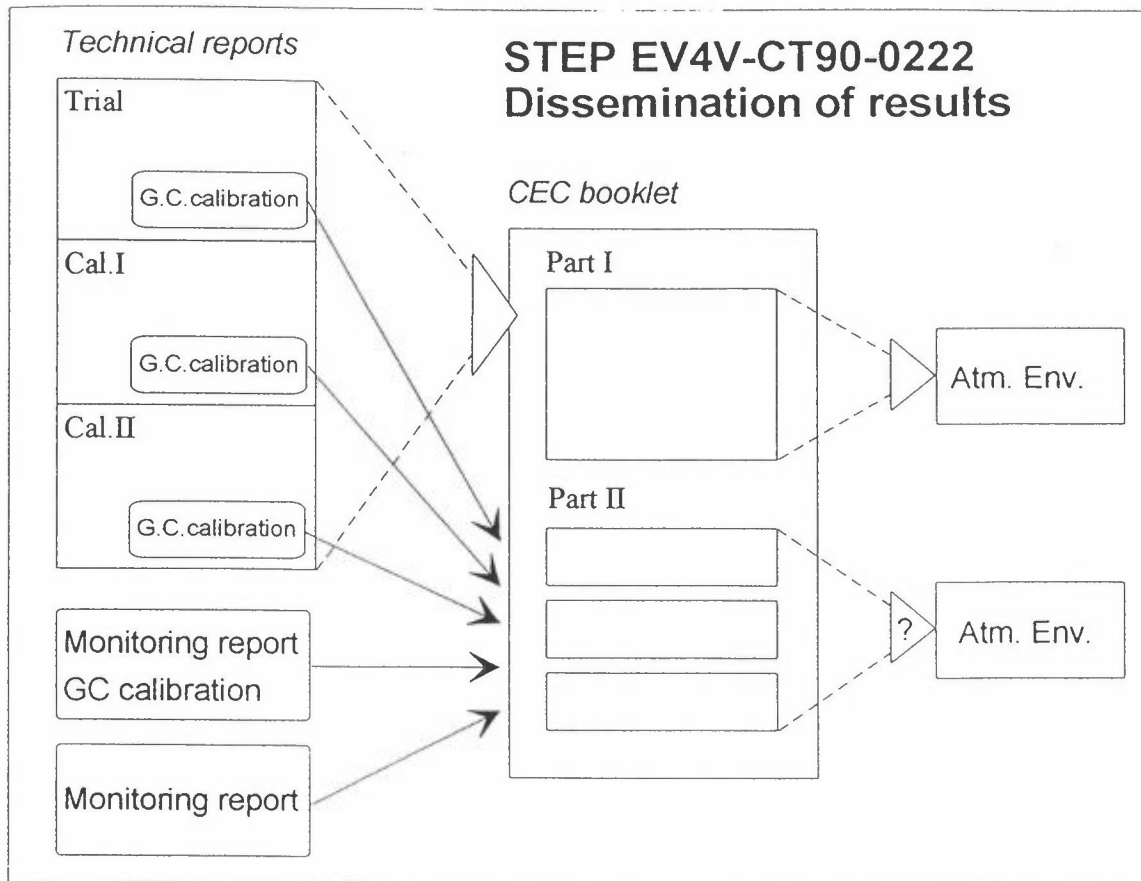


Figure 1: Plan for dissemination of results in two steps; a CEC report followed by publication in a reviewed journal.

#### 4. Conclusions

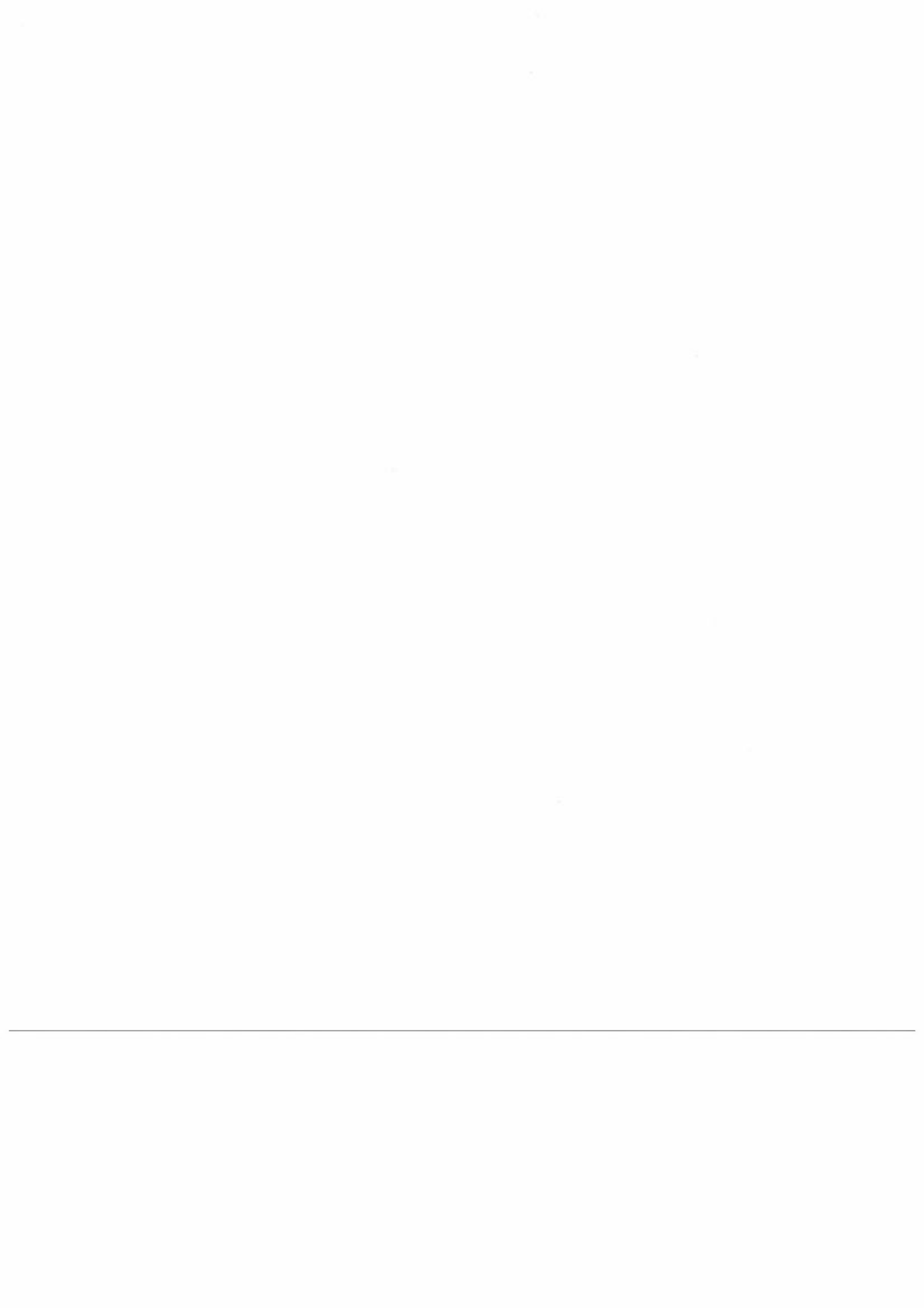
For the first time, PAN solutions have been distributed to a group of participants situated all over Europe.

It has been demonstrated that the PAN solutions are stable within  $\pm 15\%$  or better over a period of 8 months, with transports and normal use between initial calibration and re-calibration.

The largest errors in calibration of the PAN standards found during the project are  $-80\%$  to  $+200\%$ . The distribution of solutions has made it possible to identify such outliers, and reduce the errors to  $\pm 15\%$  for  $100 \mu\text{g PAN / ml}$  solutions, and  $\pm 25\%$  for  $10 \mu\text{g PAN / ml}$  solutions.

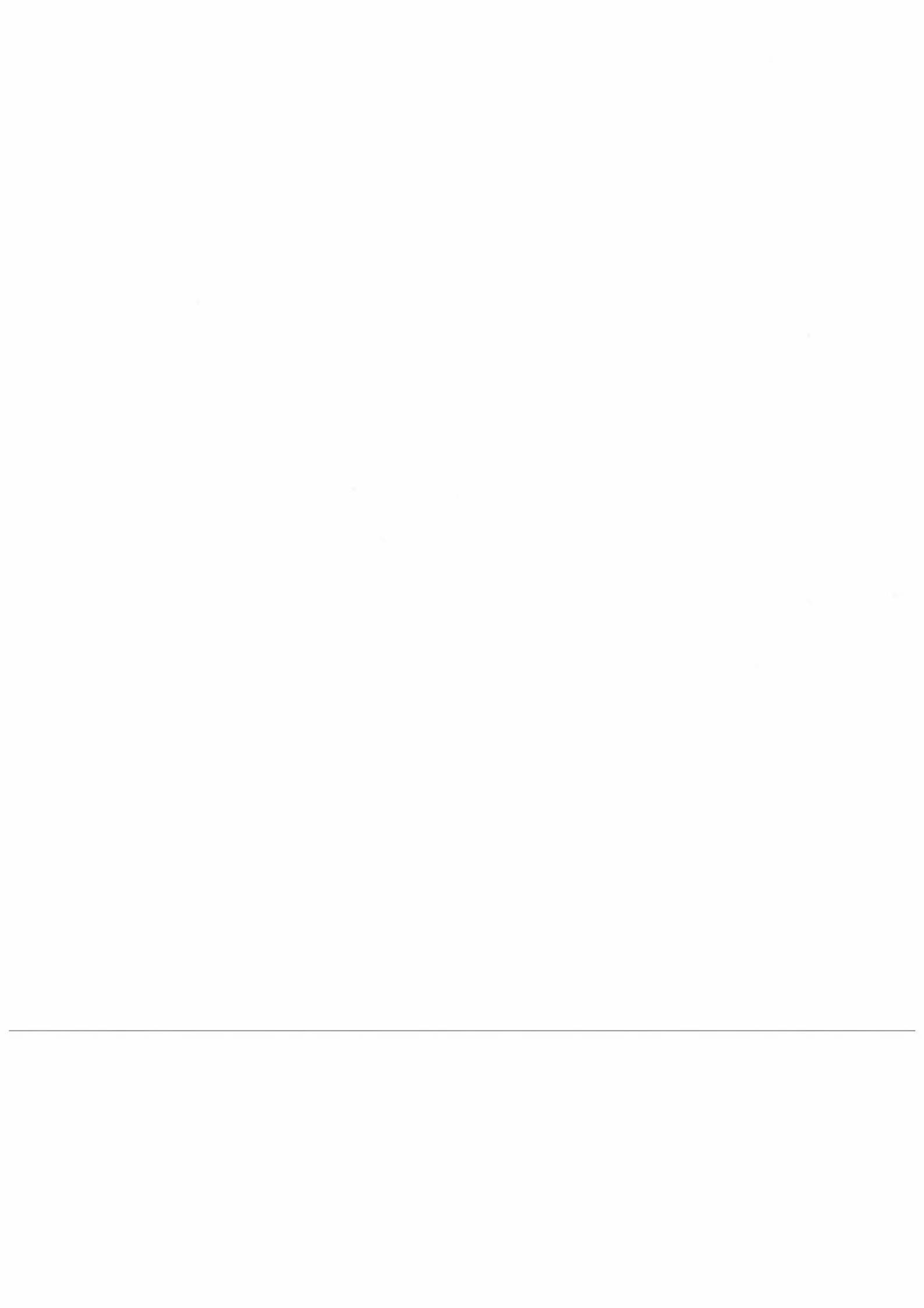
The project did not have the means to perform a similar comparison of PAN GC calibration methods. A field intercomparison of GC calibration and GC response to ambient air will be proposed in 1995.

A set of ambient PAN monitoring data is available. The group will co-operate with modellers to increase the value of this data set. Also data sets for the next years should be supplied to modellers. For this purpose the formation of a common European PAN database is under consideration.



## **Appendix 1**

**NILU (Co-ordinator)**





Norwegian Institute for Air Research  
P.O. Box 100  
N-2007 Kjeller, Norway

EV4V-CT90-0222  
Peroxy Acetyl Nitrate Intercalibration  
Final administrative report  
Terje Krognnes  
June 1994

## **WORK PERFORMED AND RESULTS OBTAINED**

As co-ordinator, NILU has compiled the cost statements and progress reports required by the contract. NILU has transferred the economical support from the CEC to the participants, and performed the administrative tasks required to organize the project work. NILU has compiled the internal technical reports after each project phase.

NILU prepared detailed method descriptions for ion chromatographic for ion chromatographic determination of PAN by analysis of acetate and nitrite + nitrate. NILU also described all details of the dangerous goods and customs formalities connected with air transport of PAN solutions frozen in dry ice.

PAN solutions were distributed from NILU to the participants in three round-robins. NILU purified PAN solutions by HPLC and diluted the solutions for the three distributions. The solutions were calibrated by ion chromatography before distribution and after return of control samples to NILU. The solutions of the second distribution (phase CAL.I) were accidentally contaminated by acetic acid before distribution, the other solutions were of high purity. All the calibration results are reported in the technical reports.

The method for ion chromatographic determination of PAN after alkaline hydrolysis was refined during the project, so that both acetate, nitrite and nitrate may be resolved in a single analysis.

Due to PAN GC malfunction, ambient monitoring of PAN was performed at the Birkenes station in southern Norway only some periods of 1991 and 1993. The problems were found to be related to dry carrier gas. The difficulties were finally resolved by adding humidity to the carrier gas in a low concentration. Ambient PAN and PPN monitoring has been performed continuously from the beginning of 1994 with high accuracy and a detection limit of approximately 10 ppt.

---

NILU has taken part in three project meetings. The first was arranged at NILU. the two others were arranged in Rome and in Paris. During the preparations and the execution of the project, T. Krognnes of NILU has visited all participating laboratories except the University of Patras and the AEA Harwell. These visits to other laboratories have been very important for learning details of the different methods that have been employed in the project.

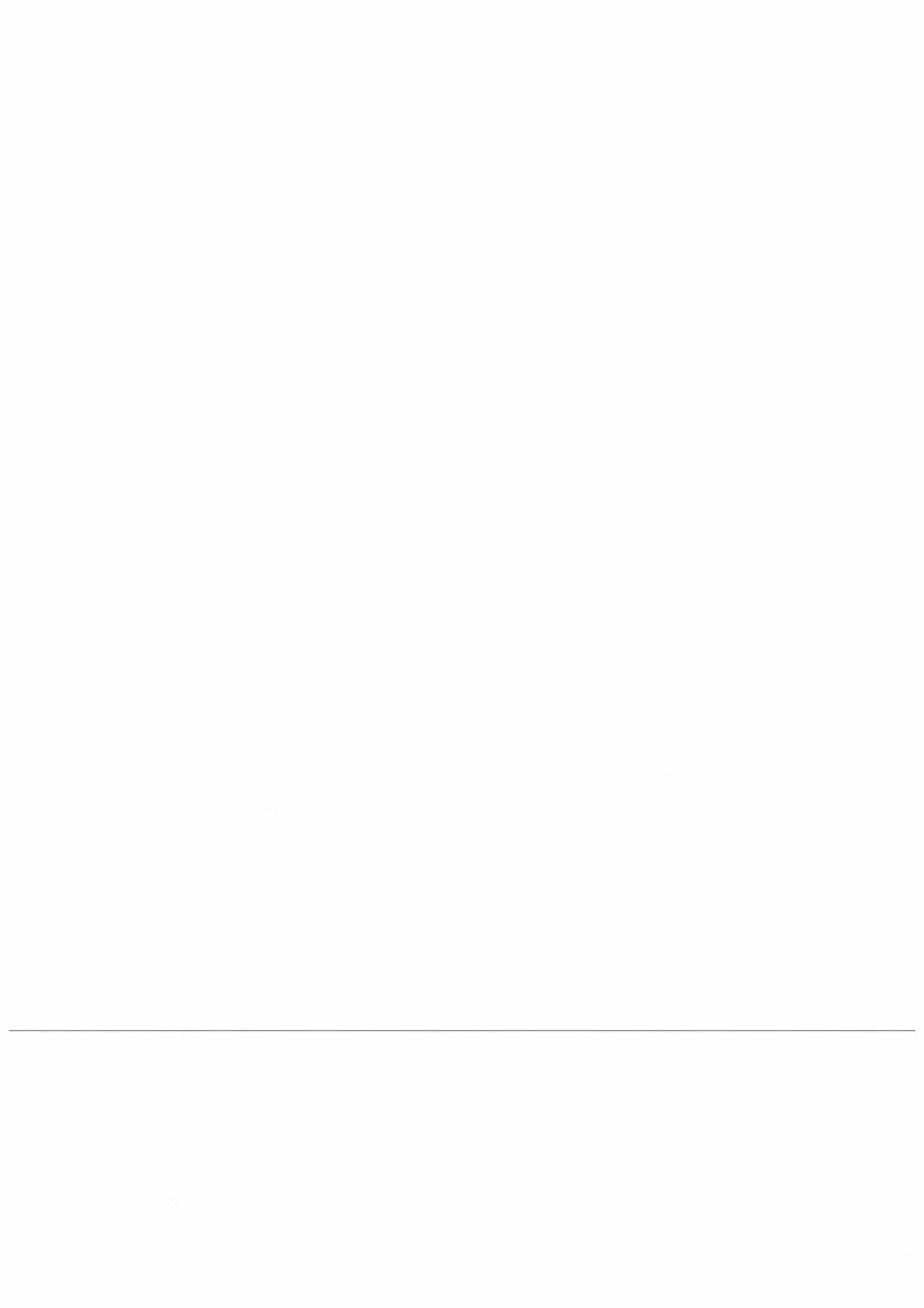
A PAN calibrator based on a diffusion tube was constructed, but could not be tested properly during the project due to the malfunctioning PAN monitor. The optional task of bringing a stable PAN analyzer around to the participants was not possible within the technical and economical limitations during the project period.

## **FURTHER WORK**

NILU will continue in the role as coordinator until the publication of the results has been completed. The group has agreed to apply for a new CEC project to arrange field intercomparisons of PAN monitors and GC calibration methods. NILU will act as co-ordinator in the preparation of the project proposal.

## **Appendix 2**

**University of Paris XII**



UNIVERSITE PARIS XII  
61 Av. du Général de Gaulle, 94010 Créteil, France

P. COLIN, G. TOUPANCE, M. MAILLE, M. JAFARI

Decembre 1993

STEP-PAN program

FINAL REPORT

#### 1- Analytical techniques for solutions of PAN in hexane :

Analysis of liquid solutions of PAN in hexane has been performed by alkaline hydrolysis and subsequent determination of the concentration of resulting acetate and/or nitrite ions, under the following conditions :

Hydrolysis: 0.5 ml of PAN in solution in hexane, adequately diluted if needed before, and 4 ml of 0.01N sodium hydroxyde aqueous solution are introduced into a 10ml flask. Concentration of sodium hydroxyde has been chosen as low as possible in order to minimize the need of neutralisation of the residual alkalinity before injection into the ion chromatographic column. The volume of sodium hydroxyde solution has been reduced to 2ml in the latest experiments in order to minimize the interference of sodium ion with the acetate ion peak when using ion chromatography. Tests have shown that hydrolysis of PAN is quantitative within the time of the experiment when using this set of experimental conditions.

Analysis: after 30mn of hydrolysis, the flask is filled up with a reagent which depends on the analytical technique used, Saltzman or ion chromatography.

Saltzman technique : the flask is filled up with Saltzman reagent and the UV absorption of the solution is recorded at 540 nm, after 30mn. Calibration is done by use of known solutions of sodium nitrite.

*Ion chromatography:* in the first experiments, the flask was filled up with phthalic acid  $4 \cdot 10^{-3}M$  in order to drop the pH down to 5-6 for preservation of the column. However, this addition of phthalic acid was suspected to introduce a big drift of the base line which was observed in the region of elution of nitrite and nitrate ions. For that reason, the addition of phthalic acid was suppressed and the flask was filled up with pure water. The buffering capacity of the eluant was sufficient to prevent any degradation of the column. The eluting solution was made by adding  $Na_2B_4O_7$  to phthalic acid  $4 \cdot 10^{-3}M$  until obtaining a pH of 3,4. Column is a Vydac 302IC, and the flow rate of eluant was 1ml/mn, increased later to 2ml/mn. Detection is made by conductimetry. Acetate is eluted first, just after the injection peak. Nitrite ion is well eluted as well as nitrate ion.

Alternative technique : it was proposed at the beginning to test also calibration by IR determination of gaseous samples. In fact, this was not done due to the little quantity of PAN available in the samples

## 2- Results :

2-1: Both techniques of measurement of PAN through nitrite ions, Saltzman and IC, resulted in very similar results.

2-2: Measurement of acetates on our IC system was much less reliable than nitrite ions. In addition, it appeared during the STEP PAN experiment that acetate is formed during the spontaneous decomposition of PAN during inconvenient storage situations: after hydrolysis, acetate ion appears to be a rather conservative parameter which, as a consequence, is not a good indicator of the actual concentration of PAN.

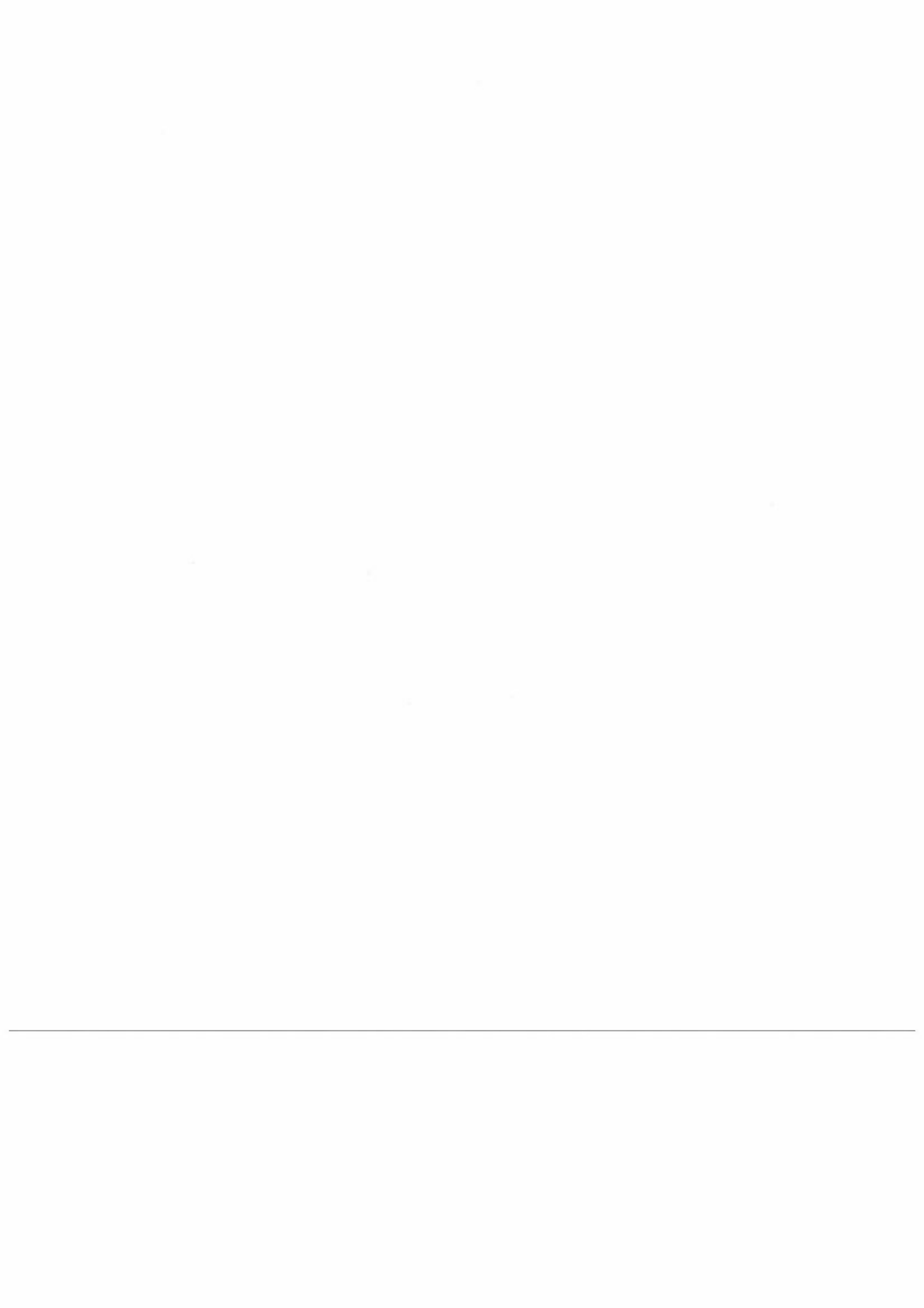
2-3: With our IC system, the determination of the most diluted solutions ( $10 \mu g/ml$ ) was not very reliable due to sensitivity problems and of some noise on the base line. This could be solved of course by using a very up to date instrument. However, this gives an interesting information within the framework of the STEP-PAN program : the objective was to test the possibility of good calibration of instruments all over Europe, with in mind the possibility of introduction of PAN monitors in air pollution control networks. For such networks, we have to take into account the reality of the equipment of the laboratories involved, all over Europe, in routine measurements and of the training of the people. It is not sure that the best IC instruments exist anywhere in these laboratories, or if they do, if they are available for PAN calibration when needed. It is the case in our laboratory where we have a very good DIONEX instrument but it is

devoted to programs not compatible with PAN calibration purposes. The simple IC we used is not expensive, easy to use and available for PAN studies. Such situations are probably not exceptional in the real world of routine measurements and our conditions are probably indicative of frequent ones. Our results show that it is not good to recommend calibration on solutions of concentration as low as 10 $\mu$ g/ml. We suggest to recommend to work on solutions of 100 $\mu$ l/ml and to dilute before use if necessary.

2-4: For the same reason, we think that the best technique is the technique that groups possesses perfectly. It is clear that measurement of nitrite ion is the best to do, acetate ion being discarded as not representative of actual PAN. However, is IC better than Saltzman? It does not seem from our results that one is better than the other, except that IC gives a more exhaustive information on the composition of the solutions. If a group is well trained in the use of Saltzman, and no easy users of IC, they must use Saltzman. If they are well equipped and trained with IC they must use it. The only important thing is that they make reliable determinations.

2-5: The calibration of PAN-GC instruments has been done by direct injection of calibrated solutions of PAN. The results were good as well as the time-stability of the instruments. However, this does not test the entire sample line and sample loop. This question remains open.

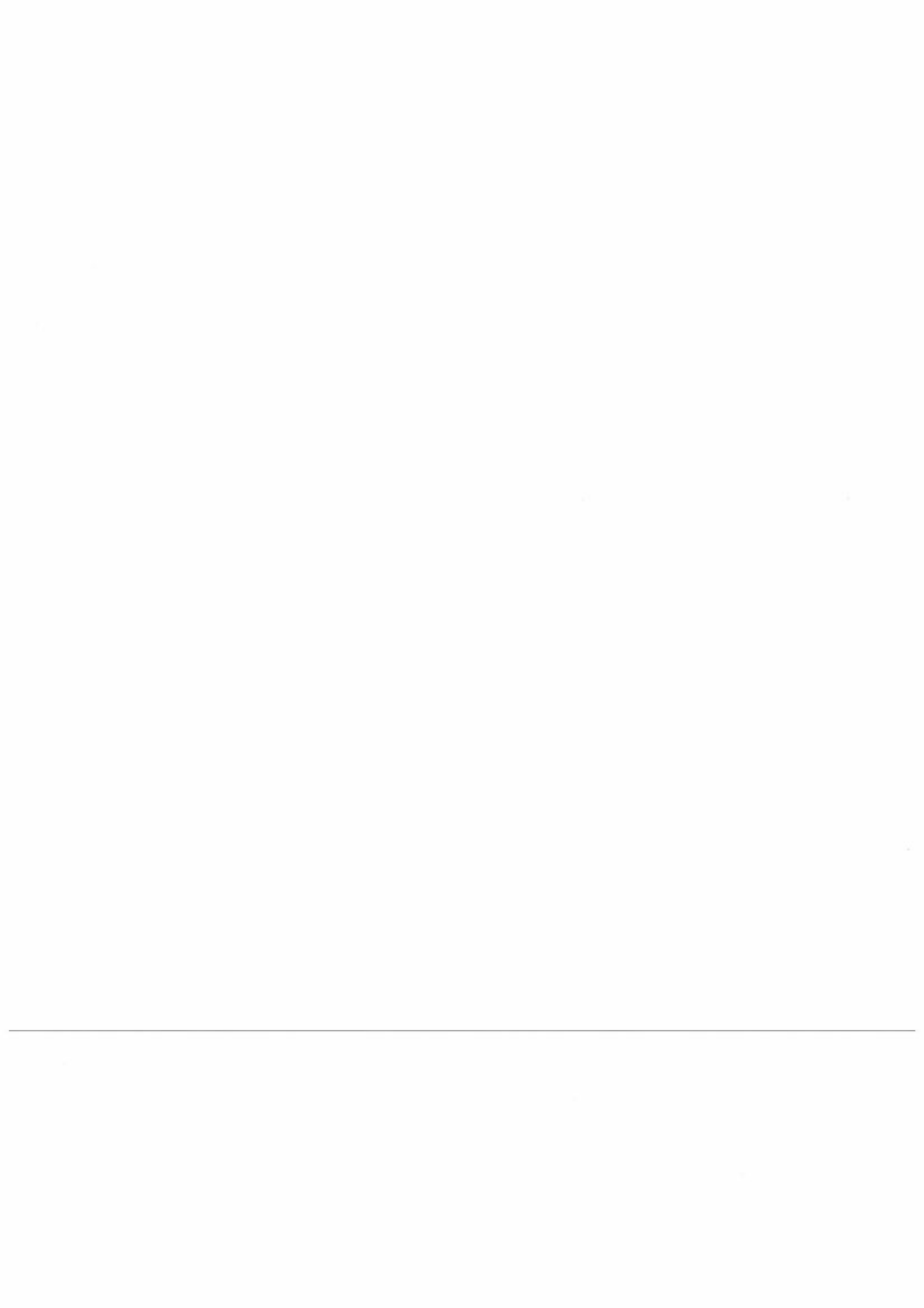
---





## **Appendix 3**

**University of Patras**



**FINAL REPORT OF THE WORK CARRIED OUT AT THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF PATRAS, UNDER CONTRACT EV4V-CT90-0222.**

Leading scientist: Dr. Sotirios Glavas  
Scientific personel : Demitrios Danalatos

**PAN INTERCALIBRATION**

**METHODS OF ANALYSIS OF PAN STANDARDS**

Depending on the concentration of the PAN standard 0.2-1 ml where taken with a pipette whose tips were cooled and transferred in 10 ml 25mM NaOH solution with the end of tips immersed into the alkaline solution, contained in an iodine flask. After five minutes the required freshly prepared Milli-Q water was added in order to obtain the desired dilution. Aliquots of the diluted hydrolyzed PAN were injected into the IC. The iodine flasks were always closed unless required. Analysis was carried out on AG4A guard AS4A column with eluants 1.8 mM Na<sub>2</sub>CO<sub>3</sub> / 1.7 mM NaHCO<sub>3</sub> for the elution and determination of nitrites, and with eluant 4.9 mM Borax for the elution and determination of acetates and nitrites. The calibration of the Dionex 4500 i ion chromatograph for nitrites and acetates was carried out using standards prepared during the analysis of the PAN standards in iodine flasks. Identification was based on identity of retention times and quantitative determination was based on the measurement of the peak height.

**METHOD REFINEMENT - DISCUSSION OF RESULTS**

At the University of Patras we analyzed all three distributed by NILU PAN standards. The obtained results according to method of analysis described earlier, as well as the average value of 11 participatants are shown in Table I.

**TABLE I  
FIRST DISTRIBUTION**

	A4		B4		C4		D4		Hexane
	Acetates-Nitrites Borax	Nitrites NaHCO <sub>3</sub> / Na <sub>2</sub> CO <sub>3</sub>	Acetates-Nitrites Borax	Nitrites NaHCO <sub>3</sub> / Na <sub>2</sub> CO <sub>3</sub>	Acetates-Nitrites Borax	Nitrites NaHCO <sub>3</sub> / Na <sub>2</sub> CO <sub>3</sub>	Acetates-Nitrites Borax	Nitrites NaHCO <sub>3</sub> / Na <sub>2</sub> CO <sub>3</sub>	Acetates Borax
Our results:									
Date: NOV 1991	95.2	-	73.3		9.8	-	7.9		
Group's mean	98.2(σ=15.9)				10.9(σ=4.1)				

**SECOND DISTRIBUTION**

Our results													
Date: AUG 92				89.5		44.0				32.8		6.0	
NOV 92		60.0							6.8				
DEC 92	56.4	59.4		43.7	59.2	50.9	18.8	8.1					12.3
Group's mean	112.2	77.0		99.9	72.5	36.1	9.5	36.9	9.6				

**THIRD DISTRIBUTION**

Our results													
Date: JULY93	103.4	84.1	78.6	87.0	82.3	94.1	10.6	9.8	9.	11.8	9.8	9.8	0
OCT 93	70.8	107.5		66.8	110.2		9.2	12.4		8.4	13.5		
Group's mean	99.4*	100.1		100.9**	102.9	11.0	11.2	11.9	11.5				

The method we had been using for the analysis of PAN prior to the start of this PAN intercalibration program, involved alkaline hydrolysis and analysis of nitrites by IC with eluent  $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ . However as the time progressed and despite many column purification attempts the nitrite peak was less and less well resolved from the system peak. During the course of this work we found out that the large negative system peak was due to the alkalinity of the solution for analysis (resulting from the hydrolysis of PAN) and not to the hexane solvent. For this reason in the second distribution we employed the on-guard filters proposed by Dionex for the use with alkaline matrices. The introduction of the on-guard filters proved to be rather problematic because their use affected the peak height and therefore this negative contribution had to be accounted for as we explained in detail in our report for the Rome meeting in November 1992 titled: "ON THE ANALYSIS OF NITRITES BY ION CHROMATOGRAPHY USED IN THE PAN CALIBRATION".

Despite the above effects and as we see from Table I, the results we have reported for the PAN standards, based on the analysis of nitrites with  $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$  eluant, are always less than the group's mean by 15-38%. Our column has now reached the point where the nitrite peak is not resolved from the system peak and for this reason we did not report PAN concentrations based on the analysis of nitrites with eluant  $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$  in the third distribution.

Following the suggestion of the coordinator from the first distribution we analyzed the PAN standards for acetates using borax as eluant. Although the results reported in the first dis-

tribution and based on acetates were satisfactory, the results particularly of the second distribution were very poor with the exception of standard D4 analyzed in August 1992. We must point out here that analyses of acetates of standard B4 carried out in August 1992 yielded an average value of 89.5 which compares well with the group's average of 99.9 but we did not report it in December 1992 because the nitrite analysis yielded 44.0 and 50.9 both in August and December 1992 and our acetate analysis in December 1992 yielded 43.7  $\mu\text{g PAN/ml}$ . We now know that the 89.5 value mentioned earlier was a correct one and the December 92 value of 43.7 was wrong.

The reason for the low PAN concentrations reported, based on the analysis of acetates, particularly in the second distribution and less so in the OCT 93 values of the third distribution, can be revealed if we examine the calibration factors extracted from the appropriate calibration graphs constructed throughout the duration of the contract as shown in Table II below:

Table II

Variation with time of calibration factors for acetates

Calibration Date	Calibration factor
21.8.92	Made for the August analysis of 2nd distribution 0.063
1.12.92	Made for the December analysis of 2nd distribution 0.099
7.7.93	0.100
15.7.93	Introduction of use of Iodine flasks 0.040
16.7.93	0.047
20.7.93	0.054
1.10.93	Made for results of 3rd distribution 0.085

$$x = 0.071, \text{ St.Dev} = 34.7\%$$

Table II indicates that when we used, on 15 July 1993, iodine flasks for the alkaline hydrolysis of the PAN standards and for the subsequent dilutions, flasks which are closed to ambient air, the calibration factor decreased to approximately half of what it was before 15.07.1993. Therefore the results of PAN reported on DEC 92 only because of the calibration factor would be half of what would had been with the calibration factor of 15.07.1993. Indeed examination of Table I, second distribution, shows that the reported by us PAN-acetates values, in DEC 92 are exactly half of the group's mean. Similarly the August 92 PAN-acetates results are ~20% lower than the expected group's mean and all the difference can be attributed to the ~20% higher calibration factor compared to the 15.7.1993 one.

Similarly in the third distribution the PAN-acetates reported in October 1993 are lower than the group's average by a factor accounted for by the respective higher calibration factor determined in 1.10.1993, despite the precautions taken.

## CONCLUSIONS

The best results were obtained with the analysis of nitrites using the eluant Borax. The calibration factors of nitrites (Borax) determined throughout the study period yielded an average value of  $0.051 \text{ cm}/\mu\text{gNO}_2 \cdot \text{l}$  with standard deviation in % of average of 17%. The second best results were obtained, the analysis of nitrites using  $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$  as eluant and despite the poor resolution of the nitrite from the system peak; these good-reproducible results are due primarily to the good repetition of the calibration factors, as shown by the standard deviation as % of average of 11%. The poorest results were obtained with the analysis of acetates and the main reason for this is the poor repetition of the calibration factor as shown by the 35% variation of the standard deviation of the calibration factors expressed as % of the average calibration factor.

Most probably contamination of the calibration acetates solutions was the major error source. Even after 15.07.1993 when iodine flasks were used throughout the acetate analysis the high calibration factor of 1.10.1993 shown in Table II indicates the contamination may be easily done.

## PAN AND OZONE CONCENTRATIONS AT PATRAS, GREECE

### Site Description.

The samples were collected 2m above the roof of the Chemistry Building, 12 meters above ground at the University campus, 10 Km north east from the center of Patras. As shown in Fig. 1 our sampling site, square, is located in the approximately 3 Km corridor between the sea and Panachaikon mountain (1926 m) about 1500 m from the shore. The existence of high mountains on both sides of the Patras and Corinthian gulfs seems to have a channeling effect on the synoptic winds; thus the prevailing wind directions are either in the sector North-East or South-West/ The NE winds are expected to advect clean air as there is no significant city or industry upwind of Patras. The emissions of the city of Patras advected to our site by the W-SW winds most probably could not be transformed to the secondary pollutants PAN and

ozone within the one hour or less time period required to travel the distance Patras-University campus at Rion. It is possible however than the night emissions of the city of Patras are transported by the land breeze to the gulf of Patras and the next day these emissions while transforming are returned back by the sea breeze. Unfortunately there is no complete meteorological study of our site and therefore the hypothesis of the land-sea breeze circulation has not been checked.

#### Instruments and calibration

PAN was analyzed with a HP 5890 gas chromatograph equipped with an ECD operating in the constant current mode. The detector was maintained at 45°C. The analytical column used was a wide-bore capillary HP-1 100% dimethyl polysiloxane gum length 5 or 10 m and 0.53 mm i.d. operated at 30°C. The injection of ambient air to the column was done automatically every 30-40 minutes using a timer actuated six port valve with a 1ml loop. The flow rate was adjusted so that PAN be eluted at ~2 minutes. PPN was also observed to be eluted in 4.5 minutes but the observed flat peak was rarely sufficient for integration. The ECD was calibrated with the distributed by NILU PAN (and NPN) standards by injecting into a PTFE Teflon bag of known volume, measured with a gas meter, a certain amount of the distributed standard. The obtained gaseous PAN mixture was connected to the six port valve of the GC and several samples were withdrawn as was done with ambient air. The ECD was calibrated from its response to the PAN concentration, calculated from the amount of the liquid NILU-PAN injected into the PTFE bag and its volume.

Ozone was determined continuously with the DASIBI model 1008-RS ozone analyzer. In addition to the internal calibration available with the instrument, it was calibrated with the gas phase titration of ozone with a known standard nitrogen monoxide carried out in a PTFE 800 liter Teflon chamber.

#### Quality control of 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.

Maximum hour and Mean Monthly PAN concentrations in ppb

Month	Maximum hour	Time of maximum	Monthly mean
May 1992	0.71	13	0.57
June 1992	0.61	12-17	0.55
July 1992	0.81	20	0.64
August 1992	0.99	13	0.82
September 1992	1.24	17	0.99
October 1992	1.06	20	0.77
November 1992	0.96	16	0.85
December 1992	0.59	11-16	0.55
January 1993	0.53	14-17	0.47
February 1993	0.64	17	0.55
March 1993	0.69	13-16	0.61
April 1993	0.82	14-17	0.74
May 1993	0.73	12-13	0.64
June 1993	0.77	14	0.65



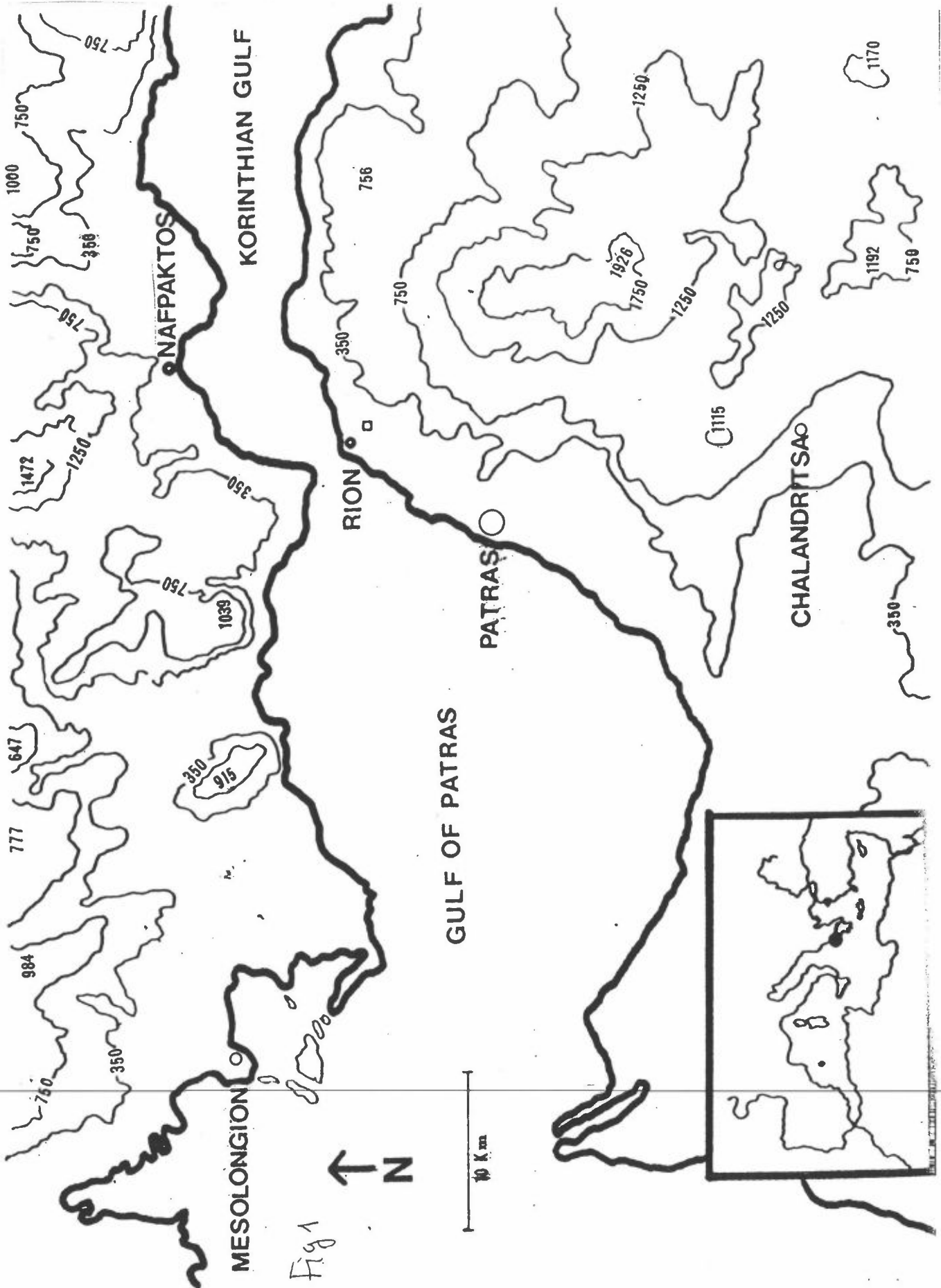
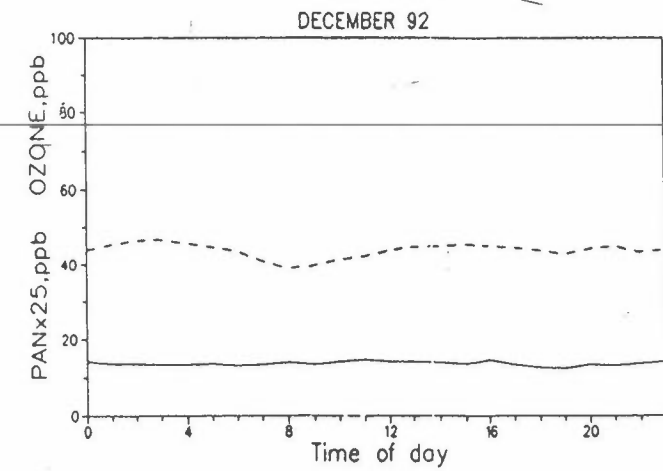
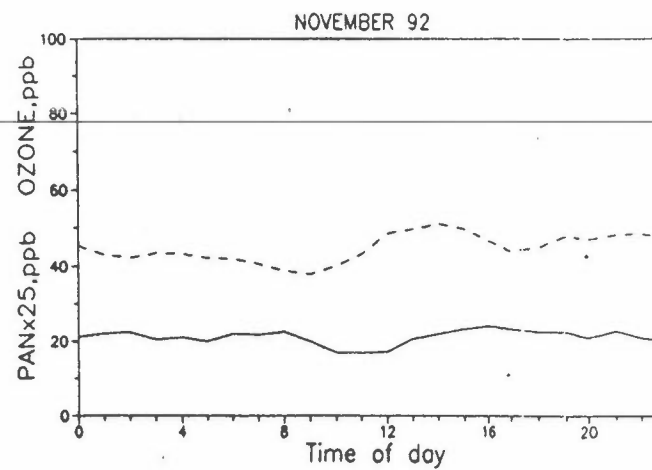
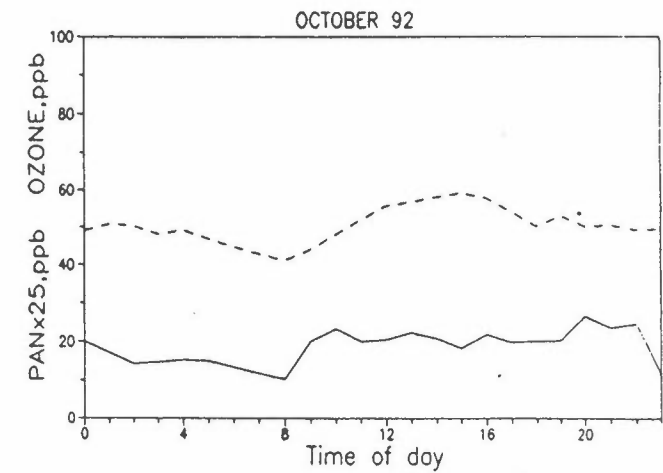
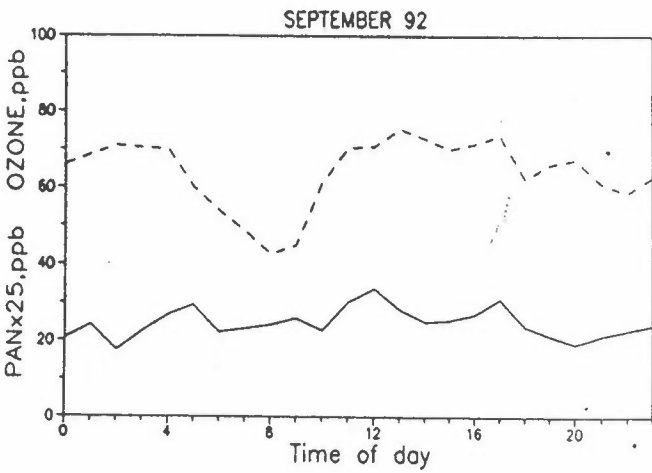
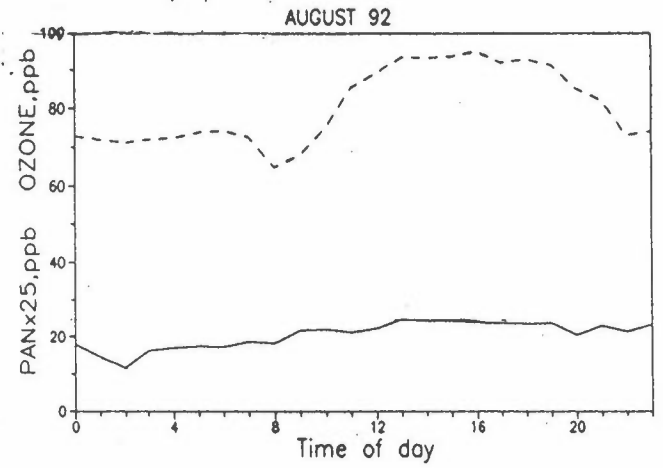
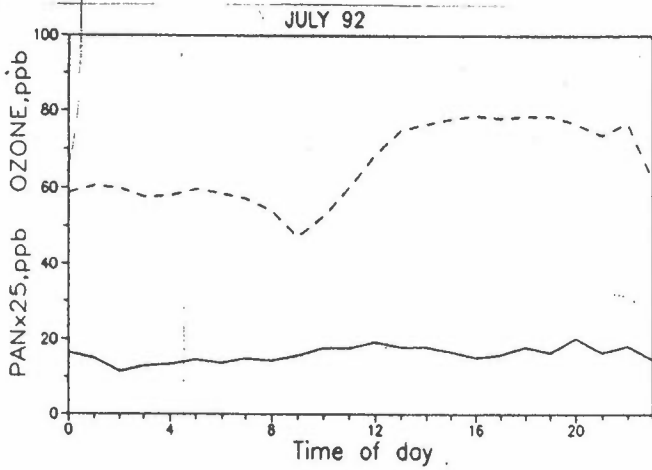
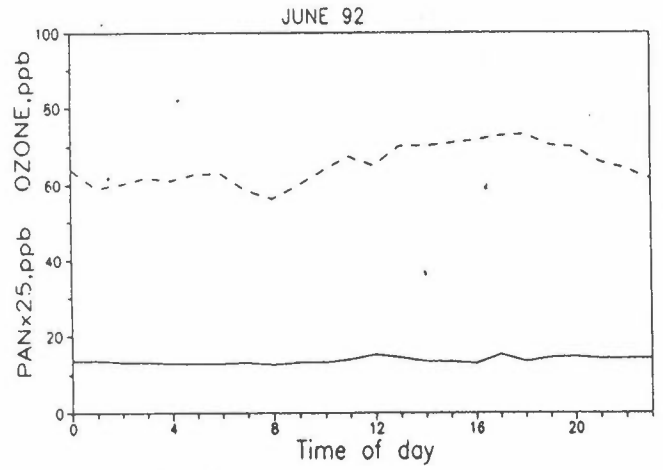
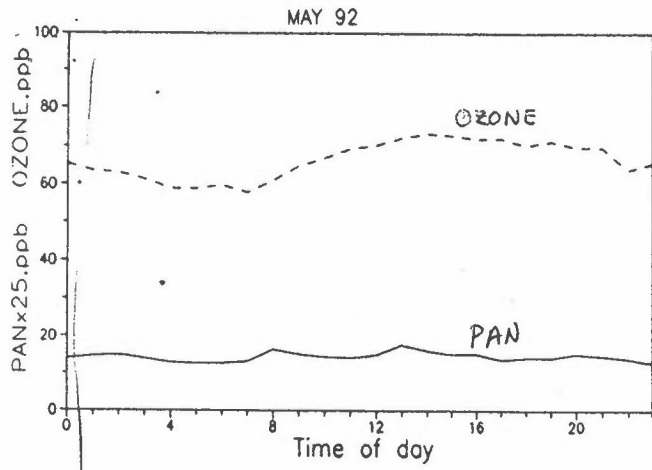
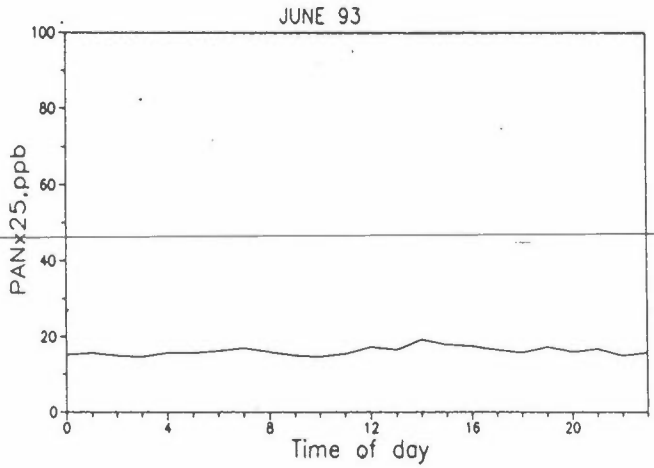
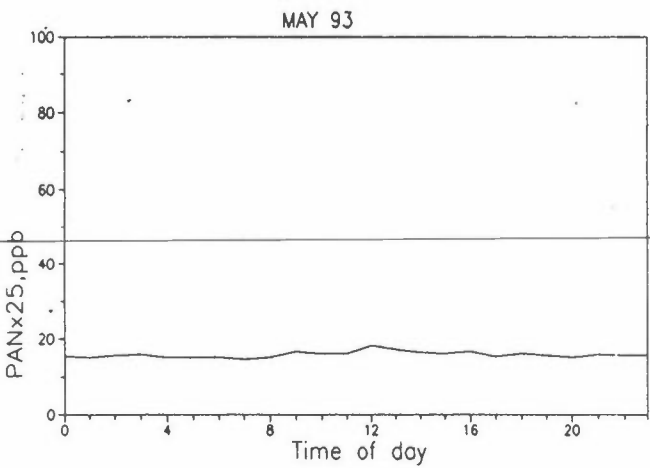
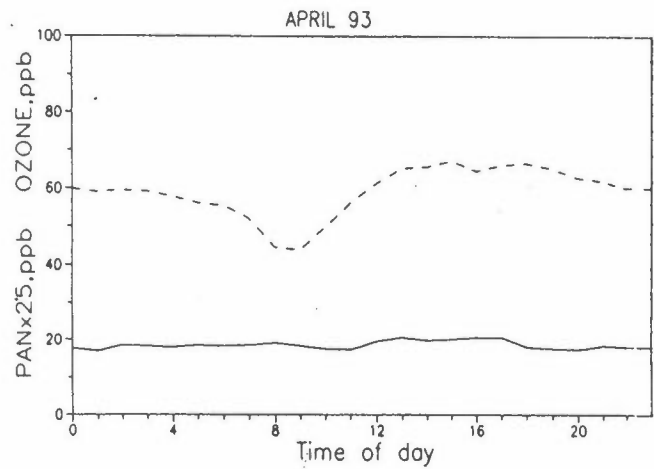
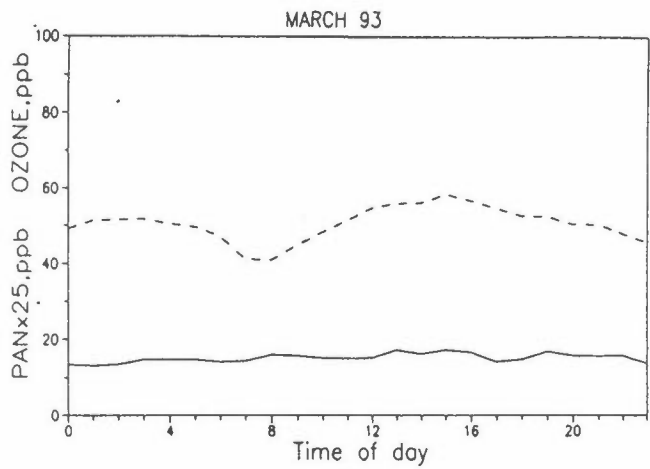
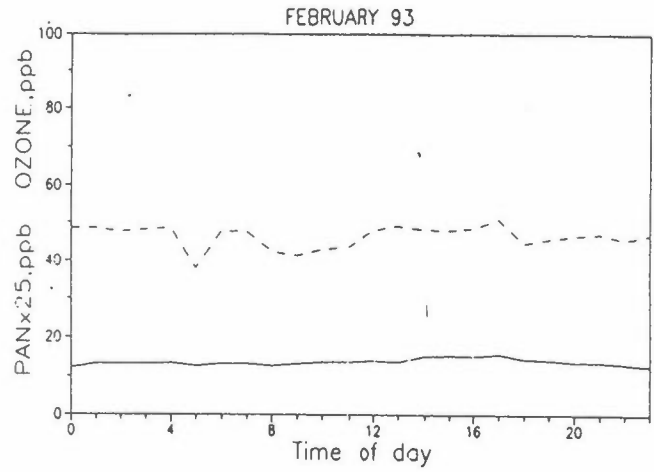
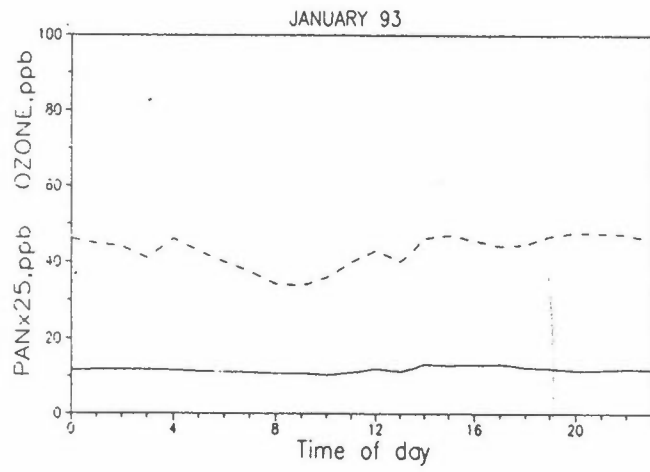
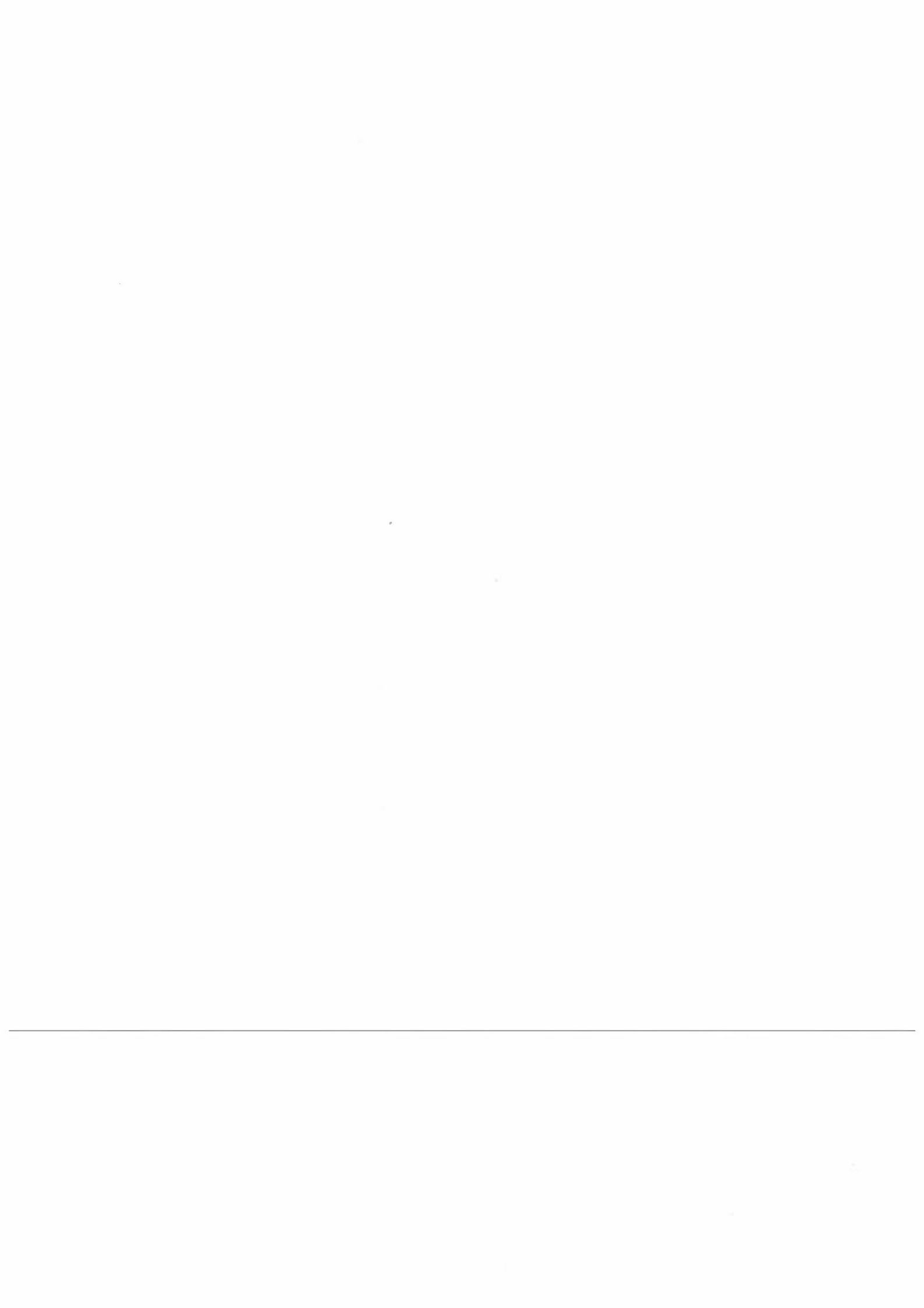


Fig 1

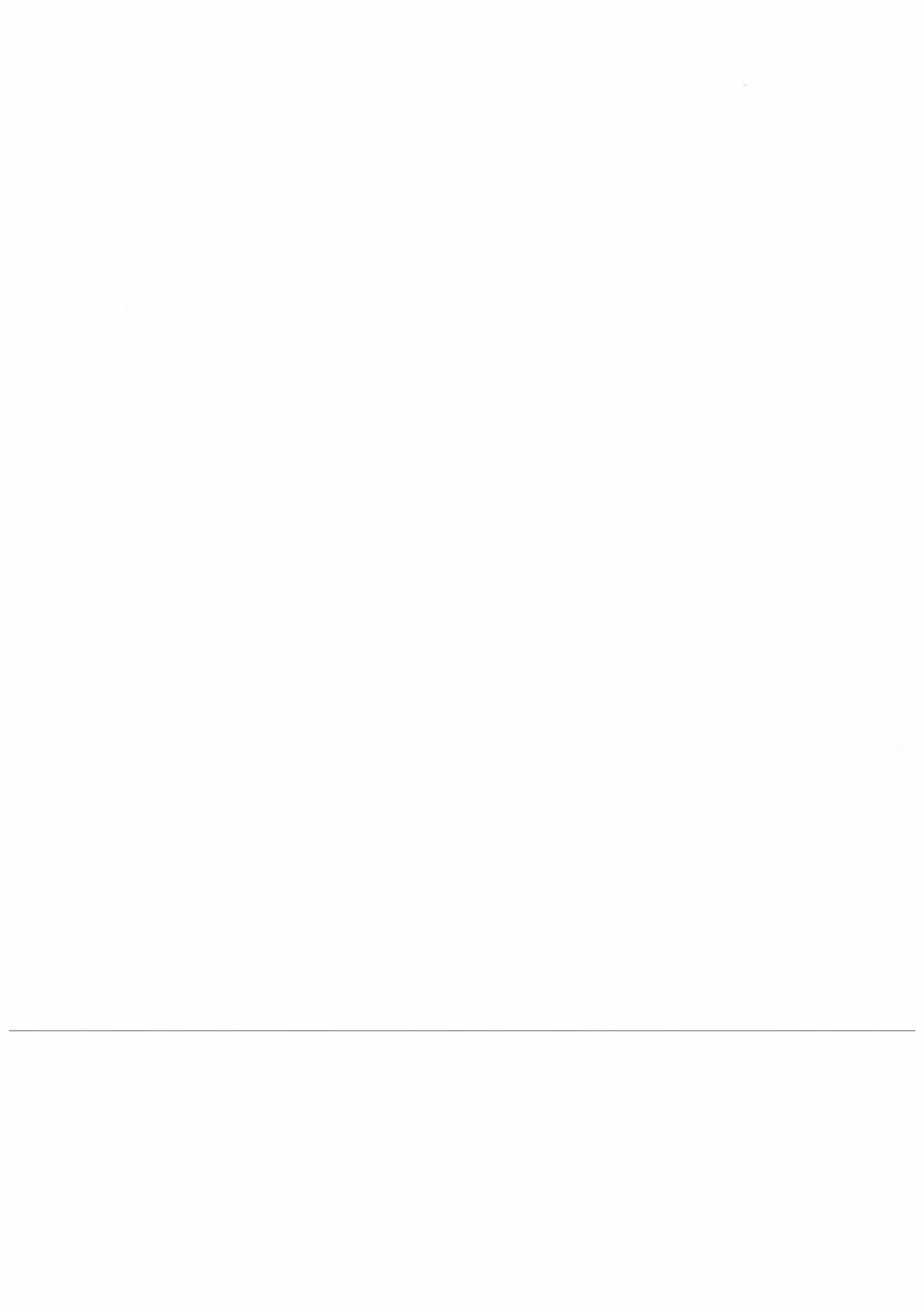






## **Appendix 4**

**TNO**



**PEROXY ACETYL NITRATE INTERCALIBRATION.**

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

This appendix summarizes the work carried out by TNO for the Peroxy Acetyl Nitrate Intercalibration project.

The project was started with the preparation of a review on the methods used by TNO for ambient air PAN monitoring and calibration of the analyzers.

Before the project started, TNO used to synthesize PAN solutions in octane for the calibration of their ambient air PAN analyzer(s). The concentration of PAN in the solutions was quantified by FTIR spectroscopy of the liquid phase.

In the preparation phase of the project we developed the method of alkaline hydrolyses of PAN solutions with subsequent analyses of the hydrolyses products, including acetate, nitrite and nitrate ions, by ion chromatography. In a latter stage of the project the ion exclusion method, initially developed for the analysis of acetate, was replaced by an ion exchange method because of decreasing performance of the former.

For each of the three intercalibration rounds of the project we analysed PAN solutions synthesized in our laboratory together with those distributed by the coordinator, using the ion chromatographic methods for the hydrolyses products, FTIR spectroscopy for the samples as such and gas chromatography (the ambient PAN analyzer at the monitoring site) after preparation of static gas phase mixtures in tedlar bags from a selection of the samples.

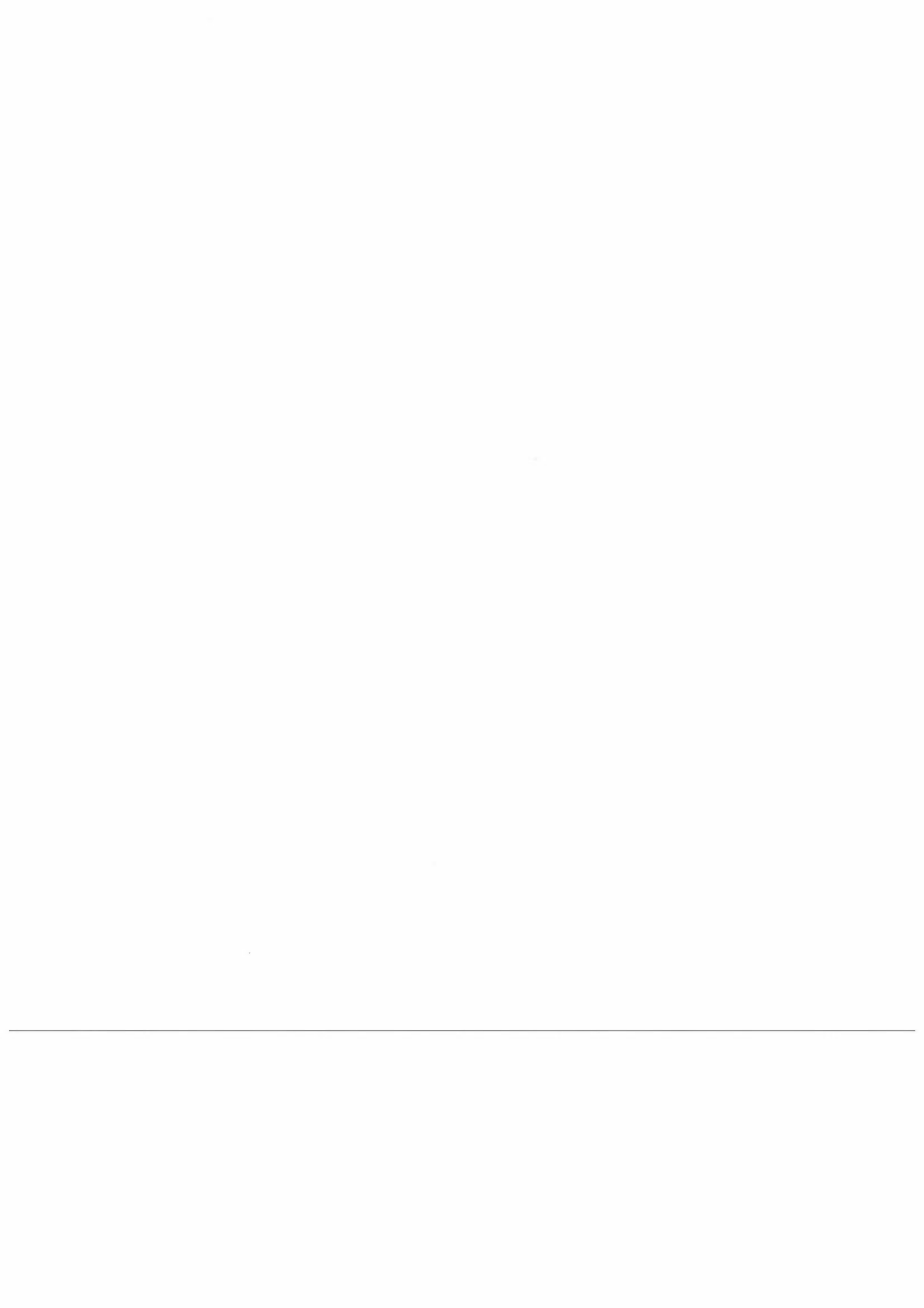
Generally in each round the series of standard solutions was analysed twice, that is: shortly after arrival of the solutions from the coordinator and shortly before return of the distributed samples to the coordinator. The number of samples and analyses in the second series of each intercalibration round was reduced in successive rounds as no deterioration of the samples during storage and handling became evident.

In the first (trial-)intercalibration a comprehensive series of analysis was carried out (multiple aliquots of a large number of samples analyzed in duplicate for each of the species acetate, nitrite and nitrate) to study the contributions of different error sources such as sampling, hydrolyses and analyses to the overall uncertainty of the results.

The analyses of nitrate was eliminated in later rounds since only minor amounts close to the detection limit were observed.

Fully automated ambient PAN measurements (four samples per hour) were set up at Kollumerwaard, a remote monitoring site in the north east part of the country. Measurements started in July 1991 and were continued up to the end of 1993. The resulting data were corrected using the results of the PAN intercalibration experiments in several periodic calibrations carried out in between these experiments.

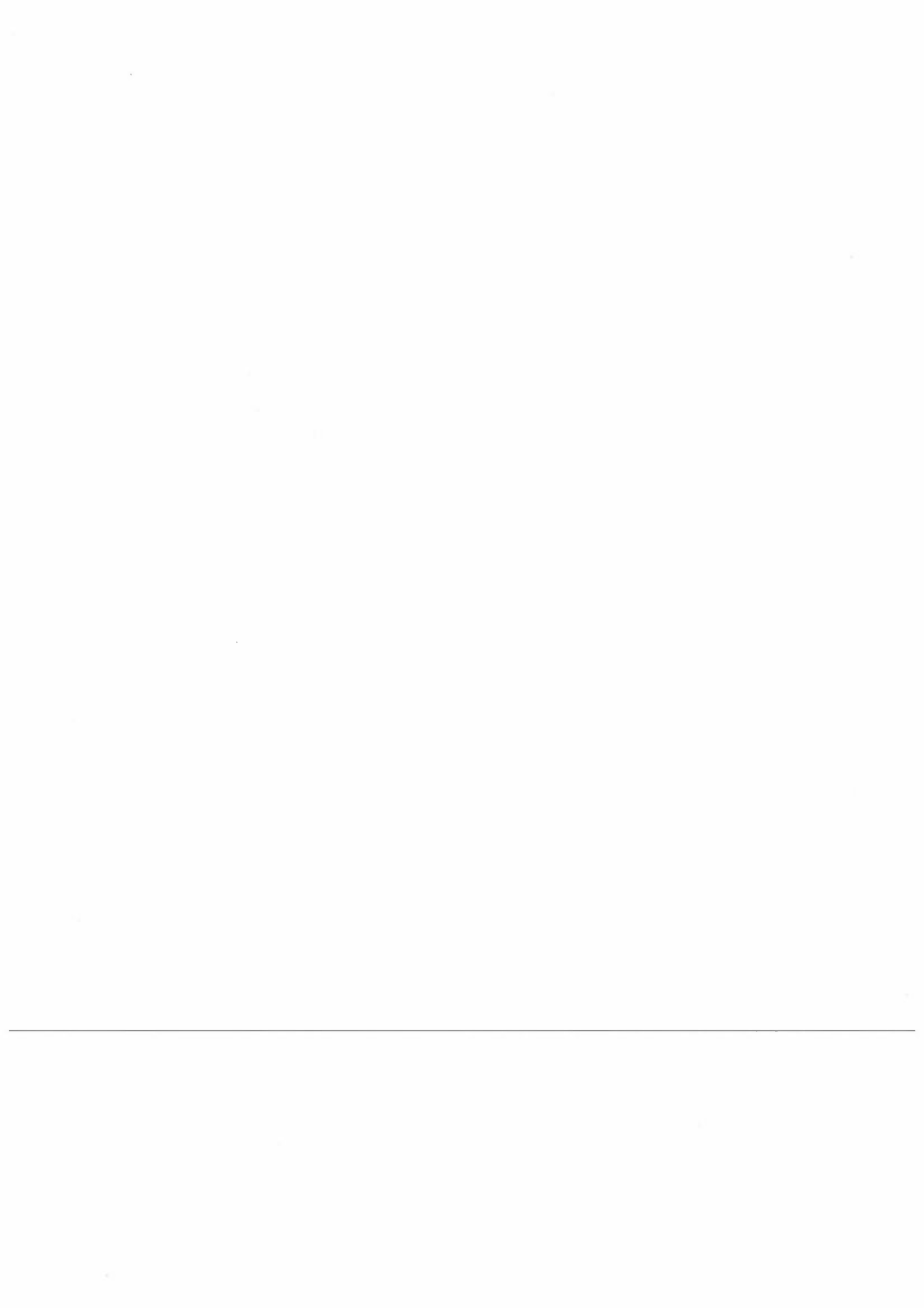
A paper with the provisional title: "PAN contribution to the photo-oxydant budget over the North Sea region" will be prepared.





## **Appendix 5**

**Meteorologieconsult gmbh**



## Activities within the EG-PAN-Project

Rainer Schmitt

Meteorologie Consult GmbH  
Auf der Platt 47  
61479 Glashuetten

### Calibration activities:

Two NILU-standards have been analyzed using ionchromatography. The results of the analysis were near, slightly above the average of all concentrations reported. All samples were successfully returned to NILU. The liquid PAN-solution no. 1 was used to determine the transfer - function from the NILU - liquid standard to our gasphase PAN-calibration for atmospheric measurements. The liquid PAN solutions was injected into the glass bulb that generally was used as reaction vessel for the photolytic production of our gasphase PAN-standard. The comparison led to remarkably good results within approx. +/- 10%. Through this additional step in the project made a direct connection of the liquid standard to our atmospheric measurements possible.

### Instrument development:

Our PAN-monitor at the baseline station IZANA, Tenerife, was not free for the numerous of experiments to be performed in the project because of our continuous monitoring program at that international station. For this reason a new GC had to constructed. We took the opportunity to change from a packed column GC to a capillary device with a sub-ambient temperature oven. The development was completed successful. The detection limit is approx. 30 ppt. We also modified our discontinuous gasphase PAN calibration device to a continuous system. A continuous NO-flux is photolytically converted to PAN. The conversion factor has been tested to be better than 95%. This new device represents a very interesting progress in calibrating PAN devices in the field. PAN is prepared in a range of approx. 200 ppt to several ppb. The device is prepared to operate automatically or controlled by a computer.

### Monitoring:

---

Our continuous measurements in the free-troposphere at the baseline-station Izana, Tenerife went on without relevant interruptions. An almost complete dataset of ppt-level PAN data for the whole period of the project has been evaluated. The detection limit of the device is approx. 0.3 ppt. In this device PAN is preconcentration at a temperature of - 83°C from a volume of

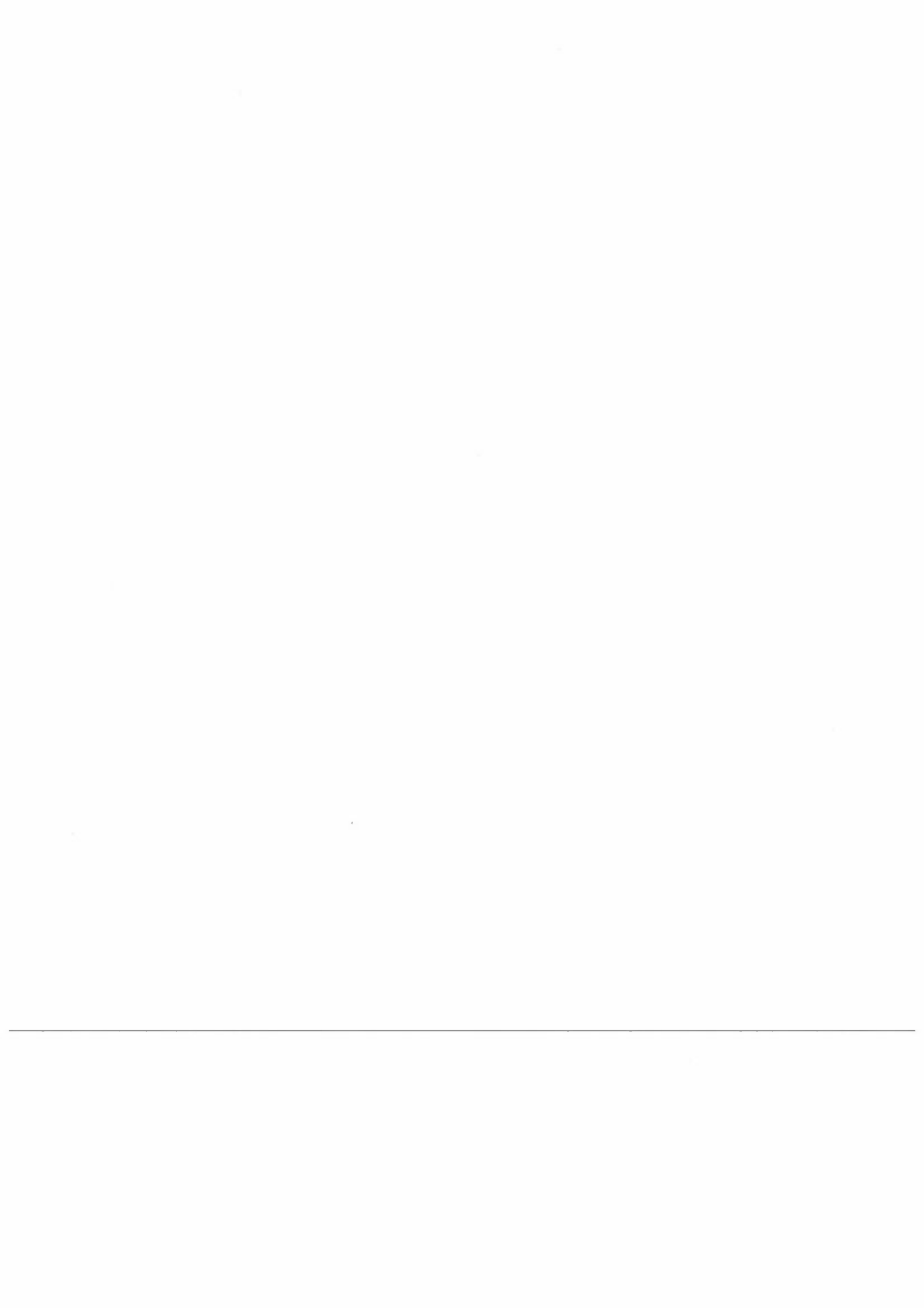
300 ml of outside air. The data are evaluated within the frame of TOR. For a period of four month, PAN was monitored with at least on automatic capillary column GC at the Umweltbundesamt near Frankfurt/Germany. Measurable PAN-concentrations were detected even in the cold season between October and December 1993.

PA0505-1

---

## **Appendix 6**

**CNR**



**REPORT OF THE ACTIVITY CARRIED OUT BY THE ISTITUTO  
SULL'INQUINAMENTO ATMOSFERICO (I.I.A.) OF C.N.R. WITHIN THE FRAME OF  
THE CEC-STEP PROJECT "PAN INTERCALIBRATION"  
(CONTRACT STEP EV4V-CT90-0222).**

Based on the Work Programme of the Project described in the Contract the following activities were performed:

- 1) Optimization of liquid and gas chromatographic techniques for the quantification of PAN standard solutions purified and distributed by the co-ordinator.
- 2) Use of these solutions for calibrating the GC-ECD based PAN Analyzers available at the Institute.
- 3) Collection of PAN, PPN and ozone data in the Tiber Valley from February 1992 to March 1994.

**QUANTIFICATION OF PAN IN LIQUID SOLUTIONS  
AND CALIBRATION OF THE FISON'S PAN ANALYZER**

**Paolo Ciccioli, Vincenzo di Palo and Angelo Cecinato**

Two methods were used for the determination of PAN in liquid standard solution: one was based on the quantification of the products formed by subjecting the original solution to alkaline hydrolysis; the other was based on the direct determination of PAN by GC. While the former method was applied to all solutions, the latter was able to provide accurate values only when the internal standard (NPN) was present in the solutions.

Alkaline hydrolysis of PAN solutions was carried out by adding aliquots of 5 mL of NaOH to variable volumes of PAN standard solutions. After some preliminary experiments it was found that 0.1-0.2 mL of solutions containing 100 ug/mL of PAN were sufficient for quantitation whereas 1 mL was necessary for more diluted solutions (10 ug/mL). The first hydrolyses were performed by using solutions containing NaOH at concentrations of 0.01 M and at room temperature immediately after the PAN solutions were taken out from the refrigerator (15-45 seconds). In the latest experiments, equal volumes of more concentrated solutions were used (NaOH 0.05 M) and the reaction was carried out by keeping the bottles in a Dewar flask filled with a slurry of NaCl and ice (ca. -15 °C). While more concentrated solutions of NaOH ensured that complete hydrolysis of PAN was achieved, lower temperatures prevented losses arising from the evaporation of sample and its thermal degradation. Checks performed by submitting to further hydrolysis the organic solution previously separated by the water solution, showed that much less than 10% of the original PAN content survived to the first hydrolysis with NaOH solutions 0.05 M. The need of maintaining the PAN solutions at low temperatures when they were out from the refrigerator was evident from the first distribution where a decrease in the PAN content in the solutions was observed as a function of the number of times the samples were taken out from the refrigerator. At the beginning, quantitation was performed by determining both acetate and nitrite ions arising from the hydrolysis of PAN. Although satisfactory results were obtained in the first distribution, we soon realized that the use of acetate could have been affected by large uncertainties due to the difficult separation with other organic ions. The quantification of nitrite was instead quite easy on our column (Dionex AS-3) being this ion well separated from fluoride, chloride, nitrate and

sulfate. Figure 1 show a typical liquid ion chromatogram of a standard solution together with those relative to two hydrolyzed samples containing PAN and NPN respectively. The separation was performed on a Dionex 4000 I chromatograph equipped with a precolumn and an AMMS suppressor. A solution containing 3 mM of  $\text{Na}_2\text{CO}_3$  and 2.4 mM of  $\text{NaHCO}_3$  was used for the separation and it was passed through the column at a rate of 1 mL/min. Aliquots of 100 uL were injected into the column. As it can be seen from the Figure no presence of nitrate were detected in the PAN solutions and no nitrite was coming from NPN. Presence of nitrate was only detected in solutions of the second distribution or in the standards that were prepared in our laboratory that were not purified by HPLC. The fact that the content of PAN we determined in the various trial distributions was quite close to the average values determined with other methods suggested that a reliable procedure was developed at the end of the project.

Gas chromatography was used to confirm data derived from alkaline hydrolysis. This was possible in our case because the PAN Analyzer (Fisons Instruments, Milan, Italy) was equipped with a liquid injector. The possibility to use GC for quantifying PAN in an unknown solution requires, however, that a constancy in the signal response is reached with the ECD and reference solutions containing PAN and PPN are available. Since the first trial distribution we tried, therefore, to evaluate the PAN/NPN ratio and check its constancy with the time. 1uL samples of standard solutions containing PAN, PAN+NPN and NPN alone were thus injected into the GC. Solutions containing 100 uL/mL were diluted (1/10 v/v) in order to obtain signals that were within the linear range of the instrument (600 ppbv). By knowing the content of PAN by alkaline hydrolysis and by checking the NPN concentration with solutions prepared in the laboratory, the PAN/NPN response factor was obtained. After the first experiments, a 1.3 ratio was measured. This value remained constant in the second and third trial distribution. It was higher than that measured in the first trial distribution (1.1) when the GC response was not optimized. This value was obtained by using the ECD in the constant current mode and by keeping the output frequency between 3 and 3.5 kHz; the column at a temperature of 30°C and the detector at 35°C. Nitrogen was used as carrier gas with a pulse width of 1 us. In these conditions levels of PAN of the order of 30 pptv could have been measured. Of coarse quantification of PAN solutions with this method is possible only if primary standards are already available and NPN is added to the mixture. The method is particularly useful to confirm the information obtained by alkaline hydrolysis, to check the content of solutions prepared in the laboratory and for evaluating whether purification of synthesized samples is really necessary. Through this procedure we found that non-purified solutions were also good for calibrating PAN analyzers as their response was consistent with the levels determined by measuring the nitrite content of the hydrolyzed sample regardless of the presence of nitrate. It is worth noting that results provided by GC were perfectly consistent with those given by ion-liquid chromatography in the second and third trial distribution.

The possibility to directly inject liquid solutions allowed the possibility to calibrate the PAN analyzer in the low ppbv range. The approach followed was to inject increasingly lower amounts of the same solution containing PAN and PPN and check both the linearity of the ECD and possible sample losses of PAN in the column. Figure 2 shows examples of the GC profiles obtained at high and low concentrations. It was found that some adsorption occurs at low mixing ratio but the decay is inversely proportional to the concentration. In general, however, a maximum adsorption of ca. 10% of PAN was measured at sub-ppbv levels with a decrease of the PAN/NPN response factor down to 1.22. Linear curves of PAN and NPN were obtained. These results were confirmed in both the second and third trial distribution. Weekly checks were performed by injecting standard solutions of NPN whereas complete calibration of the instrument was carried out every two months with liquid solutions of PAN and NPN in the range of 20, 10, 5 and 1 ppb range. Occasionally, a photochemical reactor was used for field calibrations together with NPN solutions.



During the last three years of monitoring no detectable changes in the response factor were detected indicating that a great stability was reached by our PAN Analyzer. Some experiments were carried out to quantify PPN that was always present in air sample sometimes associated with PnBN. These results indicates that response factors for these compounds were quite similar.

### MONITORING OF PAN IN ITALY

**Paolo Ciccioli, Virginio Cantuti, Angelo Cecinato, Enzo Brancaleoni, Alessandro Brachetti  
and Massimiliano Frattoni**

Several monitoring campaigns were carried out within the frame of this Project, PAN data were collected in Milan, Rome, Montelibretti and Castel Porziano. Continuous monitoring was carried out, however, only in the semi-rural area of Montelibretti located inside the Tiber Valley at 20 km North East from the city of Rome. Data of PAN, PPN and ozone were recorded together with the main meteorological parameters and they are stored in diskettes on a Quattro-Pro format. Plots reporting for each month, the hourly maximum and monthly averaged hourly concentrations were produced. An example of these graphs is shown in Figure 3. Seasonal variations of PAN were reported by plotting the maximum values, monthly averaged of daily maximum values and monthly averaged daily values. Based on the results obtained, the main conclusions of this two year monitoring can be summarized as it follows:

- 1) High levels of photochemical pollution were measured in 1992 whereas declining values were recorded in 1993 and at the beginning of 1994. Values of PAN as high as 50 ppbv were reached under photochemical smog conditions. In some instances, values of PAN were even higher than those of  $\text{NO}_x$  and  $\text{HNO}_3$ .
- 2) These levels of PAN were mainly observed during summer when the sea-land breeze circulation was carrying photochemical pollution 50 km inside the Tiber Valley. During winter time, levels of PAN were rather low ( $<0.5$ - $1$  ppbv) and they were mainly arising from long-range transport from Northern-Central Europe.
- 3) A good correlation was found with weather conditions and UV radiation intensity.
- 4) Due to the geographic and meteorological conditions, photochemical pollution was mainly a local problem restricted to those areas where big cities were situated near the sea and at the entrance of narrow valleys.
- 5) The fact that ozone/PAN ratios quite different from those reported in Central and Northern Europe were measured suggests that recirculation of pollutants and their subsidence over the sea might complicate predictions based on models.

Finally, an intercomparison field experiment was carried out together with the Spanish group in Castel Porziano. The results given by the two instruments were in good agreement.

---

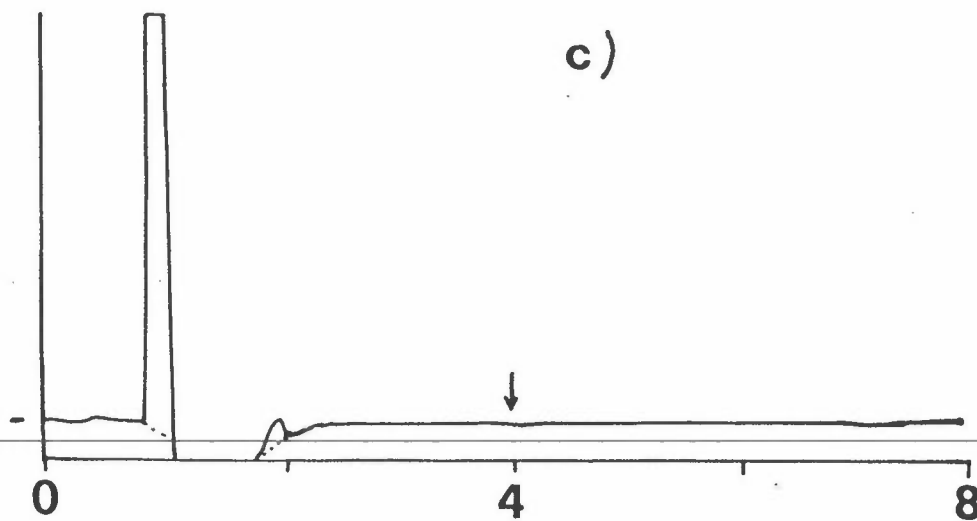
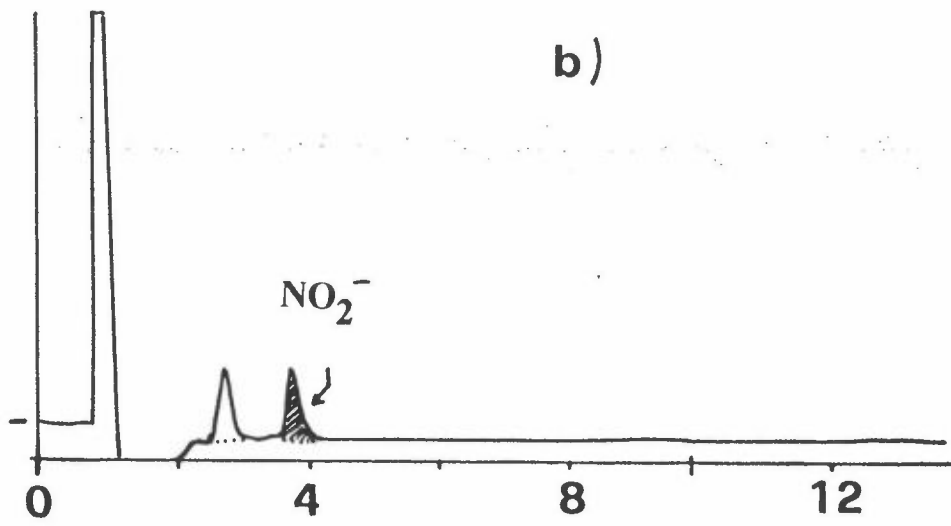
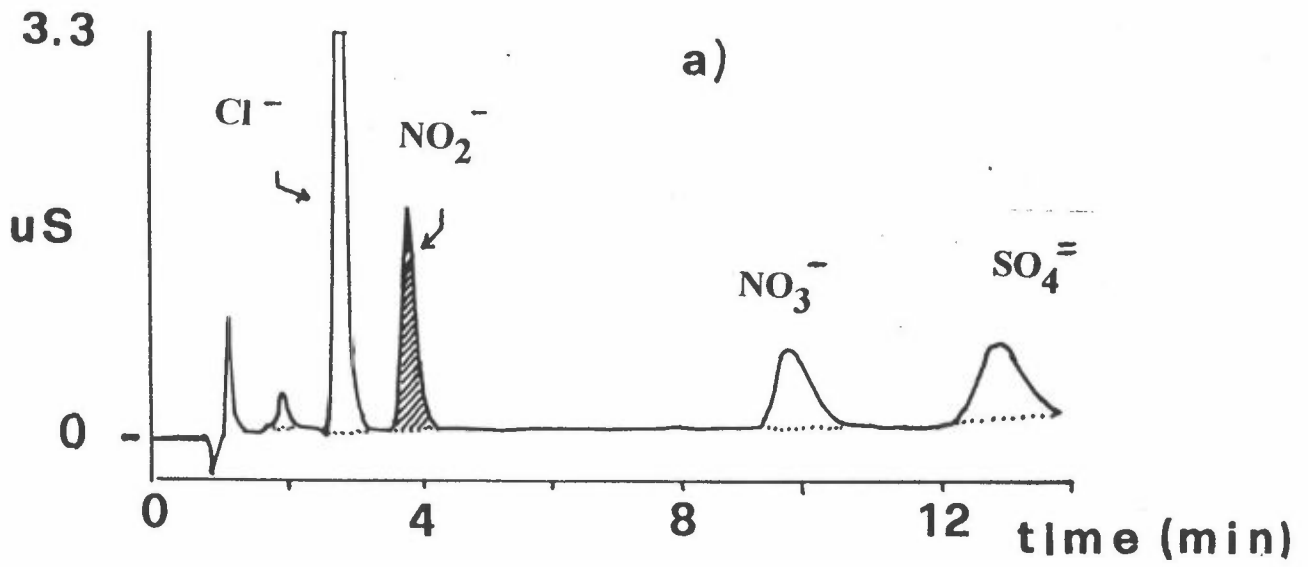


Figure 1.: Ion chromatographic analysis of solutions containing PAN and NPN (b) and NPN (c) at 100  $\mu\text{g}/\text{ml}$  levels.

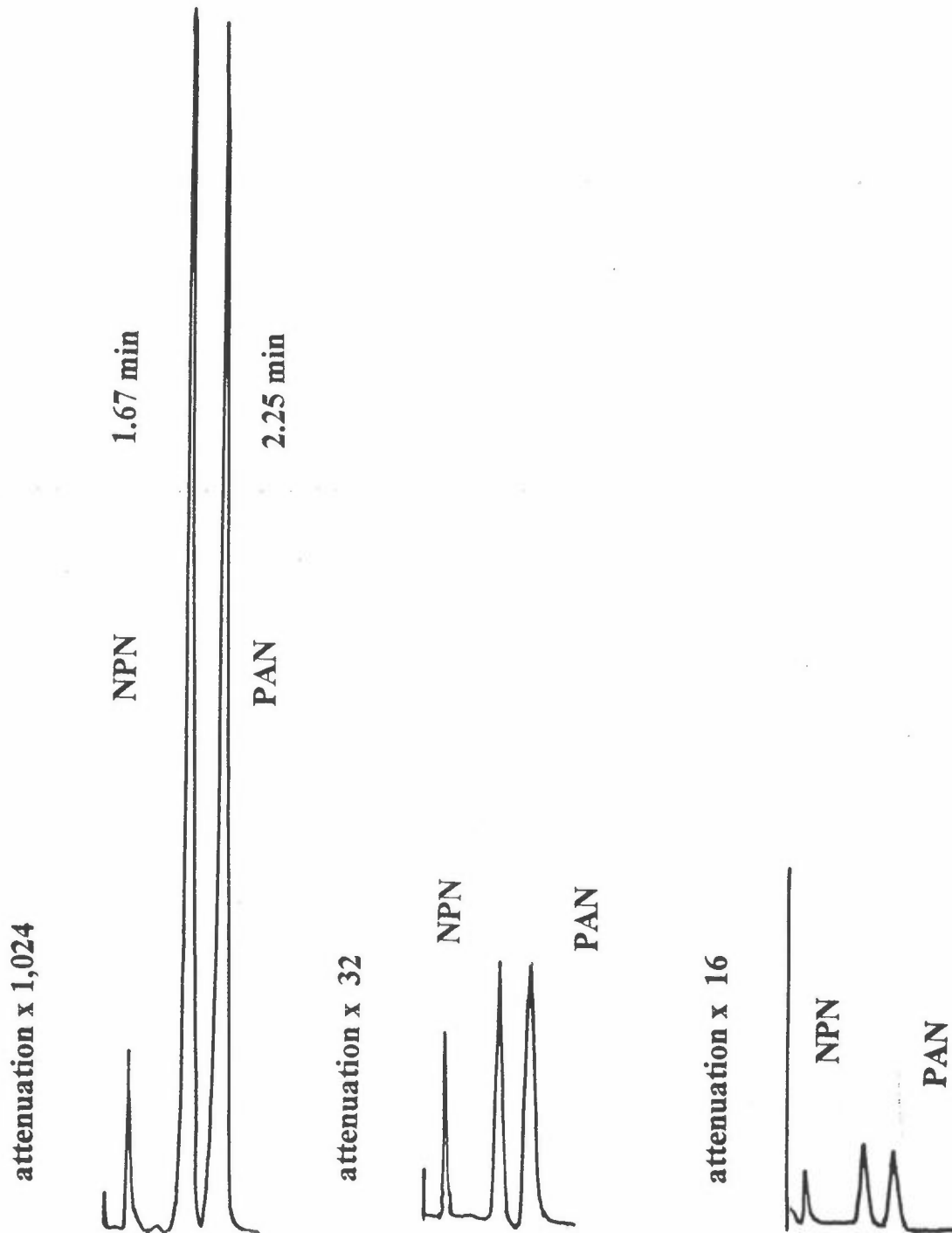


Figure 2. GC-ECD profiles obtained by injecting decreasing amounts of liquid solutions containing PAN and NPN (10 ug/mL) into the Fisons PAN Analyzer. The high amount corresponds to ca. 600 ppbv, the lowest to ca. 0.25 ppbv.

# MAY 1993

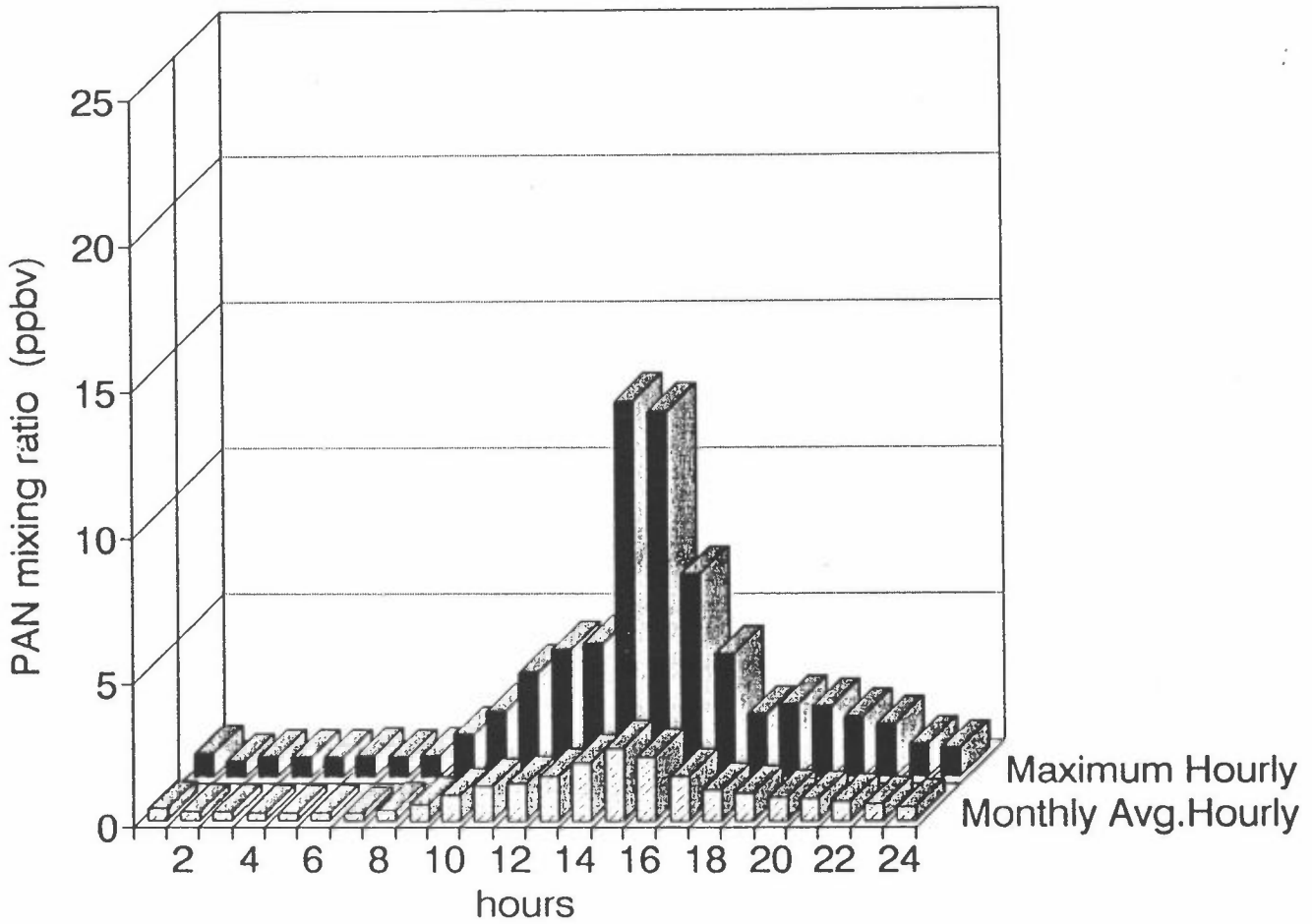
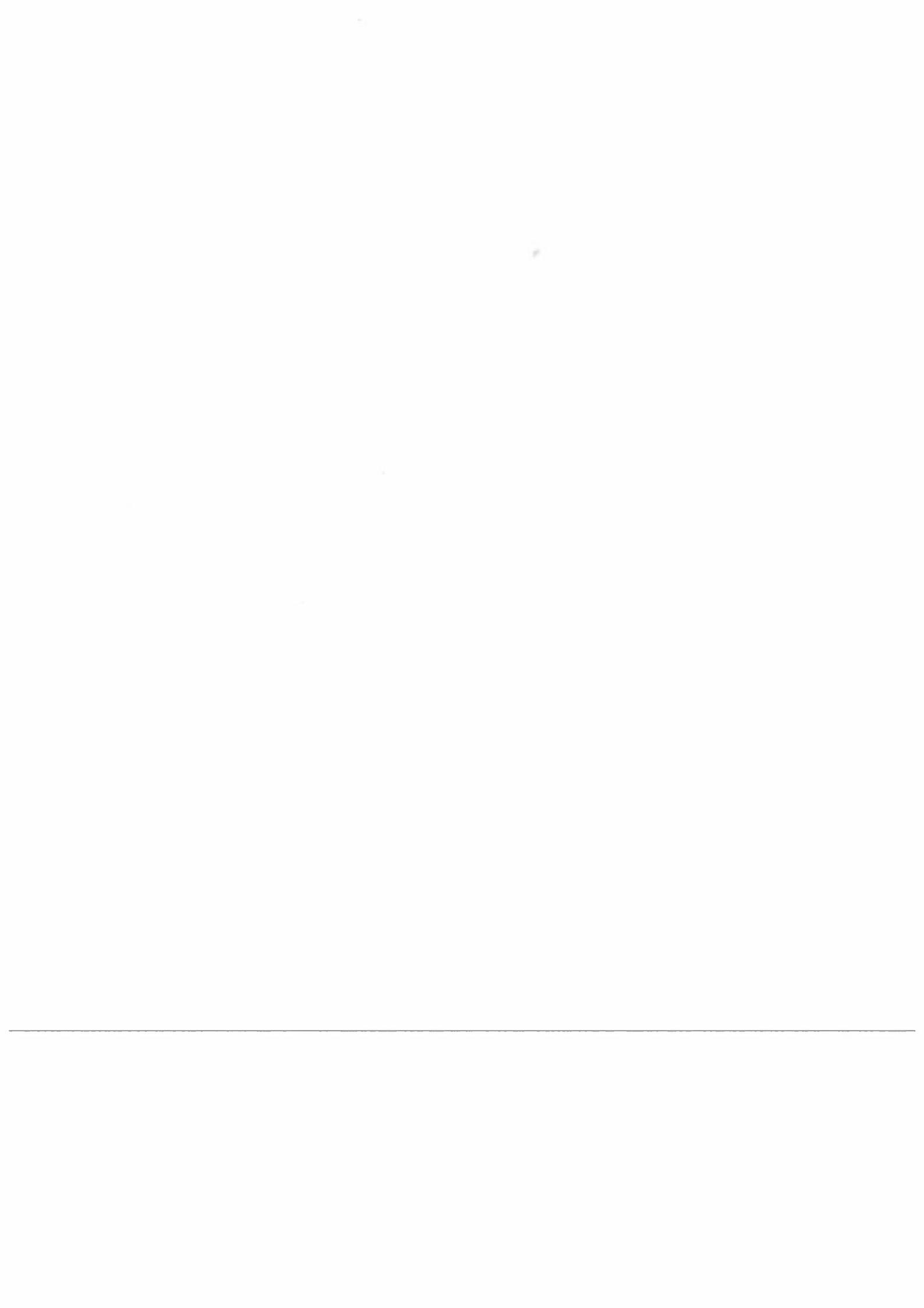


Figure 3. Levels of PAN reached in the Tiber Valley during May 1993

## **Appendix 7**

**CNSA**





MINISTERIO DE SANIDAD Y CONSUMO

INSTITUTO DE SALUD CARLOS III

CENTRO NACIONAL DE SANIDAD AMBIENTAL

The C.N.S.A. synthesized PAN in liquid solution (method of T. Nielsen, 1982) and purified the standard on HPCL.

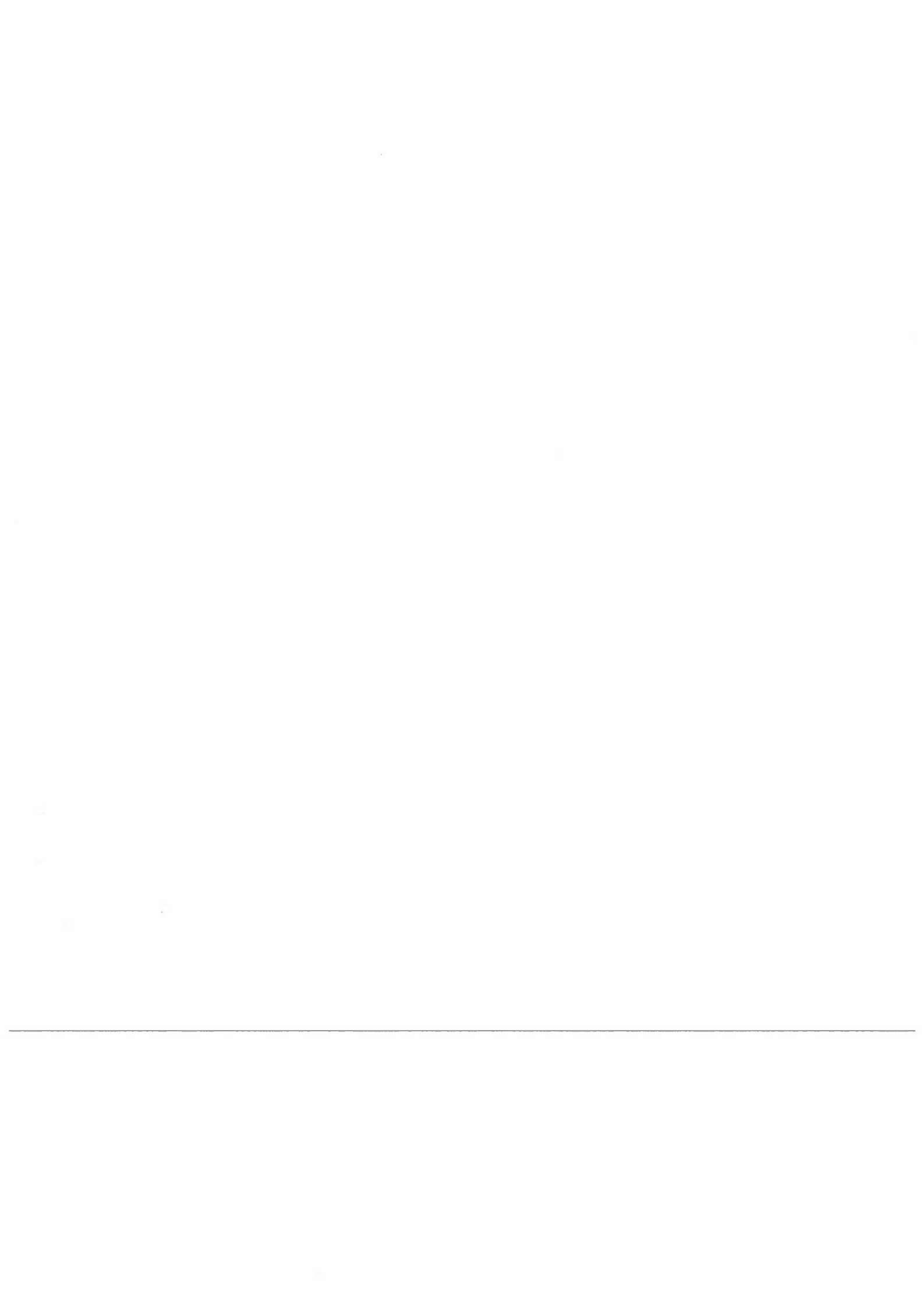
The P.A.N. standard synthesized by C.N.S.A. and other P.A.N. standards, which were sent by N.L.L.U. during this project, were analyzed by ion chromatography to determine their P.A.N. concentrations after the alkaline hydrolysis of these standards and to analyze the nitrite/nitrate concentration. These P.A.N. standards were used to calibrate the P.A.N. analyzer.

An automated P.A.N. analyzer (Carlo, Erba, Vega 6000) was located in the laboratory of the C.N.S.A. at Majadahonda, 20 Km north of Madrid, which was previously set up to continuously sample during this project.

During July 1992, the P.A.N. analyzer was located in Valbona, near the Mediterranean sea, to make a field campaign of MECAPIP project.

P.A.N. was measured in other field programmes, in Loeches, located 40 Km east of Madrid during a research project of "Formation, Transport and Deposition of Photochemical Smog Within the Madrid Area" during April 1992.

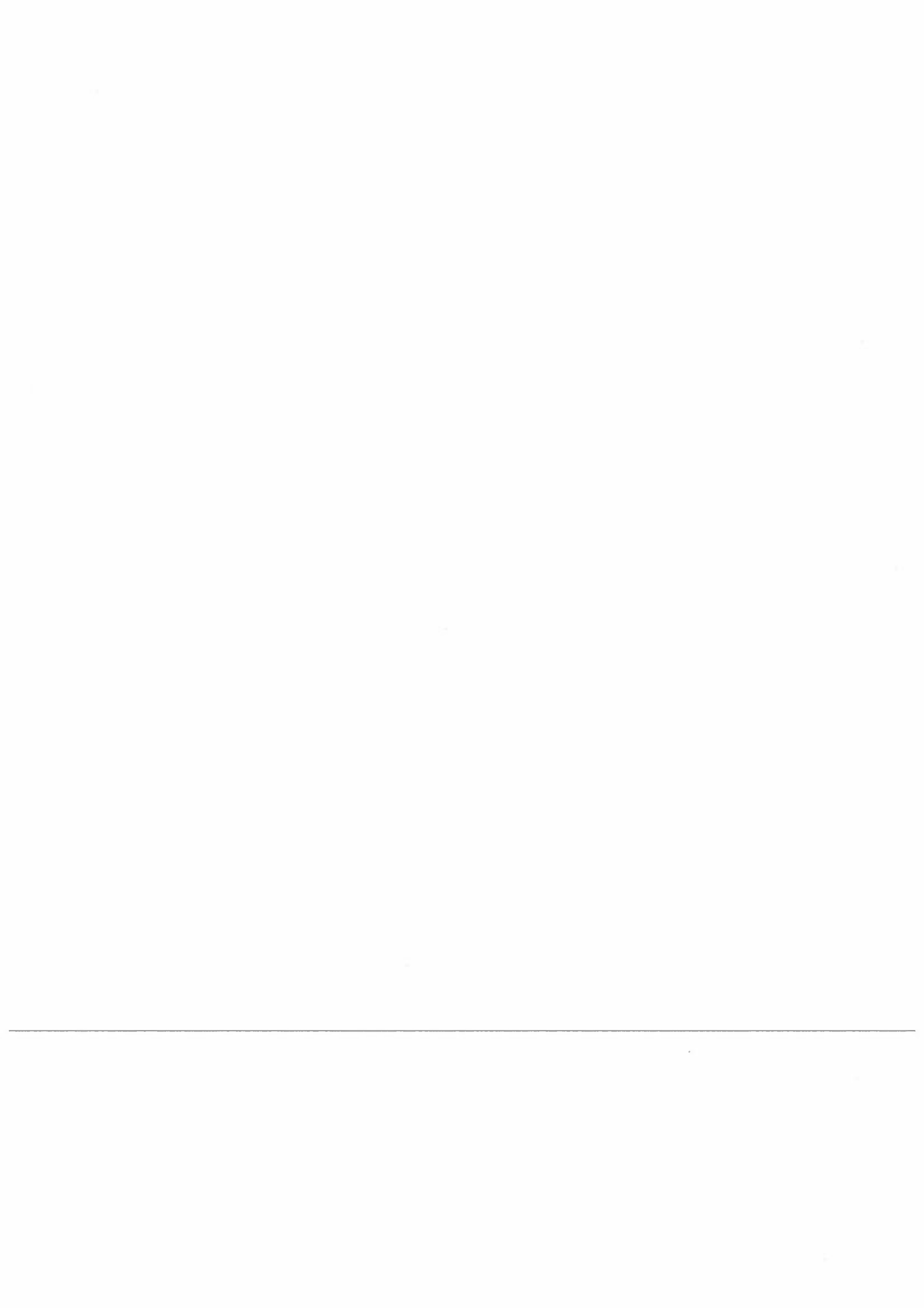
---





## **Appendix 8**

**APL (subcontractor under NILU)**



# CEC FINAL REPORT FOR THE PROJECT - STEP PAN- INTERCALIBRATION

R.Romero and P.Oyola

Institute of Applied Environmental Research - Air Pollution Laboratory, University of Stockholm, Studsvik 611 82 Nyköping, Sweden.

## *STEP PAN INTERCALIBRATION* *CONTRACT EV-CT90-0222*

### 1.- INTRODUCTION

Peroxyacetyl nitrate (PAN) is a very important compound produced by the interaction of three main components, namely hydrocarbons, nitrogen oxides and sunlight radiation. PAN is also an important indicator of photochemical pollution as well as a useful step in the understanding of the nitrogen cycle in the atmosphere and its budget.

The determination of PAN is normally carried out by gas-chromatography with electron capture detector (GC-ECD). However, the measurements and calibrations of this type of analyzers is difficult because no certified reference standards exist and they are thermally unstable.

### 2.- STEP PAN INTERCALIBRATION PROPOSAL

According to the original proposal of the STEP PAN-project, our PAN-instrument was located at Aspvreten station (at the coast 100 km south of Stockholm). This "PAN-analyzer", a prototype manufactured by the Norwegian Institute for Air Research - NILU - specially adapted for unattended monitoring of background levels of Peroxyacetyl nitrate, has supplied ambient PAN data from this background station during the project unfold.

#### 2.1.- SET UP OF THE INSTRUMENTATION

PAN was measured by an isothermal chromatograph equipped with a gas sampling valve, a packed column (silanized 1 m long, 2 mm inside diameter column) and an electron capture detector. The carrier gas - N<sub>2</sub> - with 4.8 purity, was used without any further purification traps. The operating GC-conditions were: T injector 25° C, T detector 30° C, T oven 25° C, packing material - SA-780 used most of the time (Diglycerol with QF1, 0.15% and 3% respectively). The ECD-signal was registred both in a commercial integrator (HP-3392 A) and a soft-ware "Logger 41I" (Envilogg AB, Uppsala, Sweden).

---

#### 2.2.- CONTINUOUS SAMPLING

Since February 1992 the instrument has been working for unattended routine measurements of background levels of PAN at Aspvreten, in order to create a European platform for comparison of PAN data (original Work Programme Step-PL900289, Annex I).

Besides, during February and June 1993, a Nordic Measurement Campaign of trace atmospheric species including PAN, was carried out by 5 laboratories from Sweden, Norway, Denmark and Finland, under the co-ordination of Prof O.Hov - University of Bergen, Norway.

### 2.3.- INTERCALIBRATION PROGRAMME

One of the main goals reached by the project, was to enable the participants to calibrate a PAN standard with errors within  $\pm 10\%$  of the true concentration, mainly through the TRIAL PAN standard distribution, where in our particular case, the IC acetate analysis of our laboratory has been shown to be within the expected range, without any outliers.

### 2.4.- TEST OF DIFFERENT PAN-COLUMN PACKING MATERIALS

At the strategy meeting on 3-5 september 1991, several aspects of PAN calibration and measurement techniques were discussed.

One of the point discussed was that the quality of commercial column packing materials has varied very much over the years. This is a very important step, since PAN retention in the chromatographic column depends on the ability of PAN to dissolve itself in the stationary phase, distributed over a large area of the support. Specially it is observed when a material has been found of acceptable quality; is not possible to get a similar material in the next batch of the same material from the same supplier, which keep the same properties.

This was the argument to test different packing material at the Air Pollution Laboratory (APL), supplied by the co-ordinator of the project, Mr Terje Krognes.

### 2.5.- VISIT OF THE CO-ORDINATOR OF THE STEP PAN-PROJECT TO APL, STUDSVIK, SWEDEN.

Within the framework of PAN-STEP project, a visit of the co-ordinator took place on 27-28 August 1992. During this visit, a new Electron Capture Detector Controller Module has been mounted in our PAN-analyzer. The new electronic module with a built-in facility for baseline corrections, has given substantial improvement in terms of PAN-peak and shape resolution.

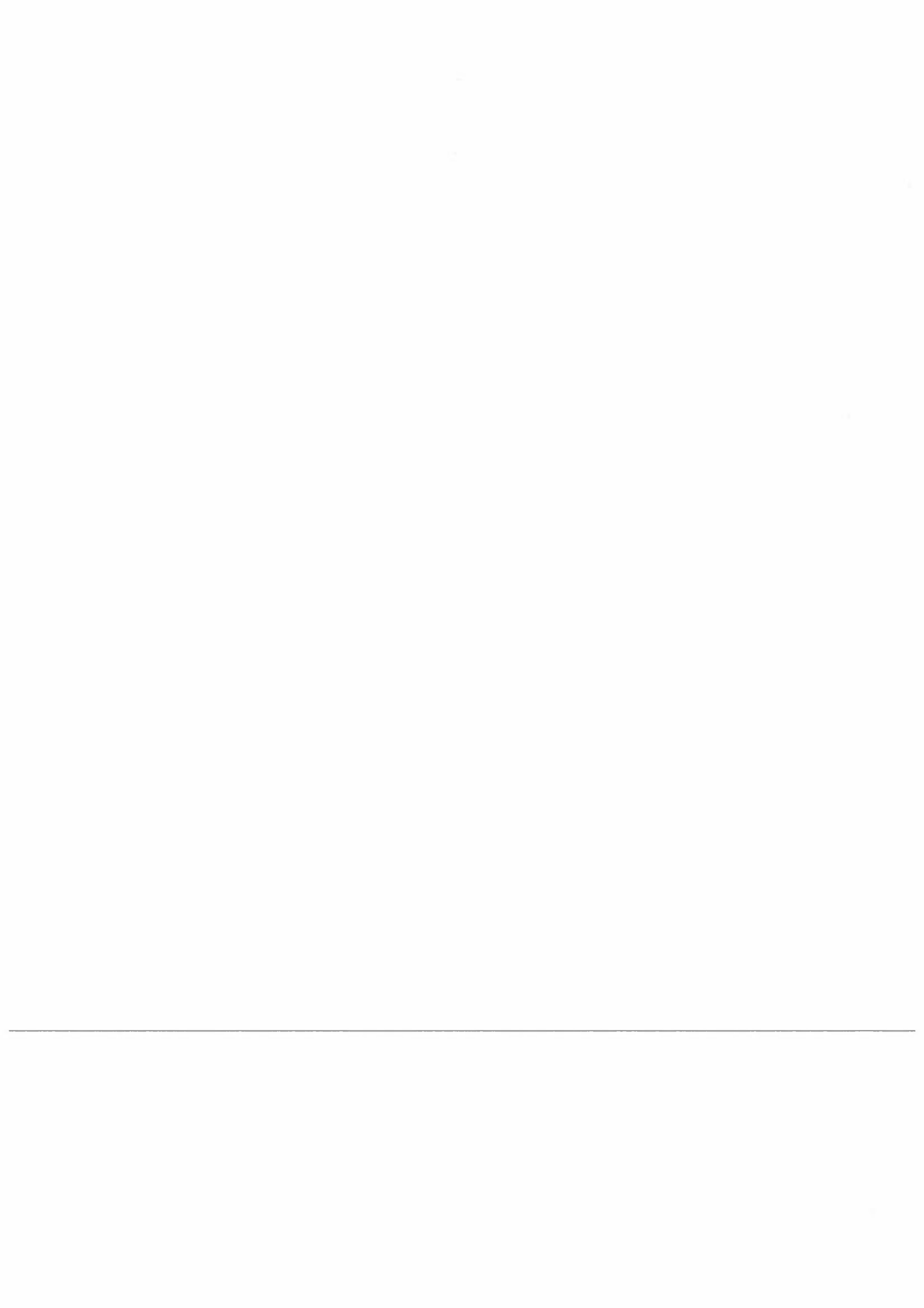
### 2.6.- TEST OF A DYNAMIC CALIBRATION METHOD FOR PAN-ANALYZER.

In accordance with the original proposal, our laboratory has successfully tested an alternative method to calibrate the PAN-analyzer in co-operation with the Norwegian Institute for Air Research (NILU), based on the use of a glass (pyrex) calibrator. This calibrator, filled with a PAN-standard liquid solution supplied by the project co-ordinator, is submerged in a cryo-bath at a predetermined temperature (between  $-20^{\circ}\text{C}$  and  $-5^{\circ}\text{C}$ ), where liquid PAN standard is diffused through the calibrator up to the PAN-analyzer detector.

The results obtained with the PAN-analyzer were also checked by parallel injections of gaseous PAN standard into a Chemiluminescence NO-Analyzer (Eco-Physics al-ppt) which was previously connected to a  $\text{NO}_2 \rightarrow \text{NO}$  Au-converter (Master Blaster). A preliminar agreement between both method is observed in a range of  $\pm 9.7\%$  deviation.

## **Appendix 9**

**KFA Jülich (independent participant co-operating with  
Meteorologieconsult**



## KFA Jülich: Contribution to PAN Intercalibration - Final Report

J. Rudolph, K. P. Müller and W. Schrimpf

Institut für Atmosphärische Chemie, Forschungszentrum Jülich, D-52425 Jülich,  
Federal Republic of Germany

During the PAN intercalibration project, contract STEP EV4V-CT90-0222, we compared several quantification methods for the determination of the PAN concentration in the liquid solutions distributed by NILU.

At the first distribution the PAN solutions were hydrolysed and their  $\text{NO}_2^-$  as well as  $\text{CH}_3\text{COO}^-$  concentrations were determined. For quantification of the nitrite ion content a modified Griess-Saltzman reaction and subsequent measurement of the UV absorption of the formed azo dye was applied. The acetate ion concentration was quantified by ion chromatography using a Dionex AS4 column, 1mM borate buffer as eluent and a  $\text{H}_2\text{SO}_4$  micro membrane suppressor. Moreover 1  $\mu\text{l}$  samples of the further diluted PAN solutions were injected into our gas chromatograph and compared to liquid injections of a PAN reference solution synthesized at our laboratory (PAN concentration also determined by hydrolysis and colorimetric nitrite ion determination).

The nitrite ion determination and the liquid injection comparison showed an excellent agreement of better than 98 % while the acetate ion determination showed values that were up to 20 % higher than the average of the two other methods.

At the second distribution the PAN solutions were also hydrolysed and the nitrite ion concentration was determined colorimetrically. Furthermore a liquid injection comparison was performed utilizing our gas chromatograph.

Additionally we compared the injected liquid samples to injected gaseous samples originating from a PAN generator. In this calibration device PAN is generated by photolysis of acetone in a  $\text{NO}_2$ /synthetic air mixture.

Again the colorimetric nitrite ion determination gave an agreement of better than 98 % with the liquid injection comparison. Our experiments showed that the PAN yield of the photolytic reaction of acetone with  $\text{NO}_2$  in the presence of oxygen is  $90 \pm 5$  %. A comparison between the injection of gaseous samples from the PAN generator with the injection of liquid samples from NILU gave slightly lower PAN values than the nitrite ion determination. Still both methods agree within the error limits of better than 96 %.

During the third distribution only the nitrite ion determination and the liquid injection comparison were applied. This time they showed deviations of up to 10 %.

Throughout the project a permeation device for gaseous GC calibration was used to check the stability and the performance of the gas chromatograph. The PAN mixing ratio in the gas from the permeation system is also determined by hydrolysis and subsequent colorimetric nitrite ion measurement.

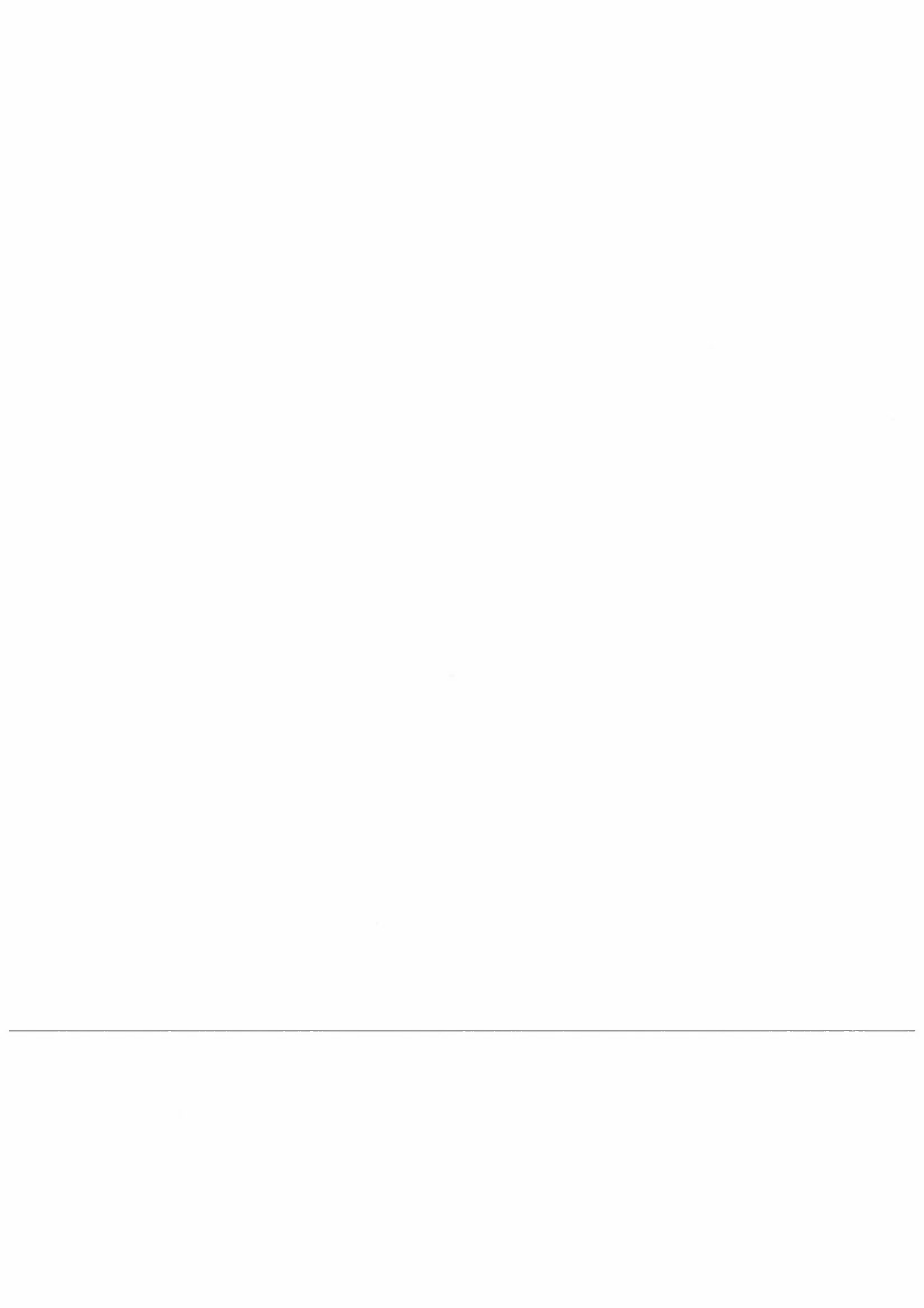
A comparison between the injection of gaseous samples from the permeation device and the injection of liquid samples from our PAN reference solution gave an agreement of better than 90 %. The stability of the PAN response in the ECD (electron capture detector) of our gas chromatograph was  $\pm 10$  % during the project. A significant reduction of conditioning effects during GC calibrations was achieved by moistening the carrier gas. Thus a faster equilibration of the measured signal from calibration gas or solutions is observed. Moreover the signal to noise ratio of PAN increases by about 40 % leading to a significant improvement of the measurement sensitivity.

---



## **Appendix 10**

**J.R.C. Ispra (independent participant)**



FINAL CEC REPORT  
PAN INTERCALIBRATION CONTRACT EV4V-CT90-0222  
ISPRA CONTRIBUTION  
Y. Libert

## ACTIVITIES

### PAN standards

- synthesis : coordinator provides participants with standards, this allows us to compare these standards with ours.
- purification : standards supplied by NILU was purified by HPLC, some of these standards was additionned with propyl nitrate, more stable compound giving a chromatographic peak near that of PAN.
- measurement of PAN content : few methods of analysis were used by participants : IR Spectrometry, Saltzman followed by visible spectrophotometry or cathodic stripping voltammetry, Ionic chromatography .In this last case study was focussed on measurement of PAN by nitrites or acetates content.
- transport : for sending and getting back standards transport was made at carbon ice temperature.
- conservation : she was made at  $-25^{\circ}\text{C}$ .

### G.C. calibration

- some different methods was used : injection of standards in liquid or gaseous state with sometime, like in Ispra control of PAN content at the last level of dilution.

### field measurements

- continuous measurement of PAN was made during about two years.

## RESULTS

### standards

- it was shown that PAN standards can be distributed and preserved without noticeable variations in content during periods in the order of several months. PAN content of standards can be determined by several methods. Participants succeeded in analysing these standards with a precision of about 15% for higher contents.
- in the case were PAN standards are not purified by HPLC and for old standards having yet evolved it is suggested to measure PAN content using nitrites content if the method used is ionic chromatography.
- we are convinced that measure of standards PAN content using nitrites content allows to avoid standard purification.

- addition of propyl nitrate permits a control of standard evolution. The ratio between response factors of PAN and nPN ( normal propyl nitrate ) depends on G.C. analysis conditions : injection and column temperature, retention time. With fixed conditions for G.C. analysis nPN can be used as secondary standard.

#### **gaz chromatographs calibration**

- calibration of gaz chromatographs was made separately by each participants, intercalibrations made simultaneously in the same place can allow to assure homogeneity of measures and to put in light problems that can occur in this field.

#### **continuous measurements**

- continuous measurement activity was foreseen to go on for one year we have measurements for twice this period.

#### **comparison between PAN measures**

- comparison of PAN measurements was made in a first time for Ispra in the regional frame defined at the beginning that is to say the mediterranean one. The first analysis was devoted to the influence of local meteorological factors and is part of the technical report given at the end of contract.

### **CONCLUSIONS**

- Distribution, analysis, preservation of PAN standards was achieved in good conditions.

- Continuous measurements of PAN was performed in several European sites for a two years period allowing a first evaluation of levels of this pollutant and of his variations.

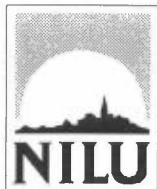
- An intercalibration of measuring apparatus in the same place at the same time would be of interest to ensure quality of measurements and possibility to compare them. This exercise was not previous at the beginning but may be foreseen.

- In the future it seems obvious that the measurements of PAN alone is without great significance and must go along not only with local meteorological data but also with measures of precursors and of significant photochemical parameters. The organisation for collection of data or their conservation in place, the form in which it seems better to keep or pick-up them and their utilization remains to debate.

---

## **Appendix 11**

**AEA Harwell (independent participant)**



**Norwegian Institute for Air Research**  
**Norsk institutt for luftforskning (NILU)**  
**P.O. Box 64, N-2001 Lillestrøm - Norway**

REPORT SERIES OPPDRAGSRAPPORT	REPORT NO. OR 23/94	ISBN-82-425-0568-3	
DATE 25.6.1994	SIGN. <i>Åorland</i>	NO. OF PAGES 70	PRICE NOK 105.-
TITLE Peroxy acetyl nitrate intercalibration Final report STEP EV4V-CT90-0222		PROJECT LEADER Terje Krognnes	
		NILU PROJECT NO. U-91051	
AUTHOR(S) Krognnes, T., NILU, Norway		CLASSIFICATION * A	
		CLIENT'S REF. EV4V-CT90-0222	
CLIENT CEC DG XII Rue de la Loi 200 B-1049 Brussels Belgium			
ABSTRACT PAN (peroxy acetyl nitrate) solutions were distributed from Norway to participants in Greece, Italy, Spain, France, Germany, the Netherlands, Great Britain and Sweden. After calibration by ion chromatography and other methods, the solutions were returned to the co-ordinator for re-calibration. The errors have been demonstrated to fall within $\pm 15\%$ for 100 $\mu\text{g}$ PAN/ml solutions, and $\pm 25\%$ for 10 $\mu\text{g}$ PAN/ml solutions. The report gives an overview of results compared with the intentions of the Work programme.			
NORWEGIAN TITLE			
DESCRIPTORS PAN	distribution	intercalibration	
ABSTRACT (in Norwegian)			

\* Classification

- A Unclassified (can be ordered from NILU)
- B Restricted distribution
- C Classified (not to be distributed)