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# STEP PAN Intercalibration

*Contract EV4V-CT90-0222*

*(CEC, DG XII/B/2)*

## ***Phase Prep. II*** ***Internal report***

Coordinator: T. Krognes, NILU



# **NILU**

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

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## STEP PAN INTERCALIBRATION

Contract EV4V-CT90-0222

(CEC, DG XII/B/2)

PHASE PREP.II - INTERNAL REPORT

Co-ordinator: T. Krognnes, NILU

Authors: Toupance, G., Univ. Paris XII, France  
Glavas, S., University of Patras, Greece  
Hollander, J.Ch.T., TNO, The Netherlands  
Matuska, P., Meteorologieconsult, Germany  
Ciccioli, P., Possanzini, M., Cecinator, M.,  
Di Palo, V., Brancaleoni, E., and  
Prachetti, A., CNR, Italy  
Libert, Y., J.R.C. Ispra, Italy  
Rudolph, J., KFA Jülich, Germany  
Krognnes, T., NILU, Norway

NORWEGIAN INSTITUTE FOR AIR RESEARCH  
P.O. BOX 64, N-2001 LILLESTRØM  
NORWAY



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## 1. INTRODUCTION

The STEP PAN INTERCALIBRATION project is an international effort to establish a common platform for calibration of PAN (peroxyacetyl nitrate) measurements in ambient air. The second project phase (phase PREP.II) involved refinement of methods previously described in phase PREP.I, a strategy meeting at NILU, and preparations for the trial standard distribution (phase PREP.III).

## 2. STRATEGY MEETING AT NILU

The first plenary meeting of the project participants took place at NILU in Norway on 4-5 September 1991. Originally, this was the only plenary meeting planned in the project, but the experience was very positive, and the group decided to arrange a second plenary meeting after phase CAL.I. Enclosure 1 contains a brief description of the proceedings, the program for the trial standard distribution (as presented by the coordinator during the meeting), and copies of some of the figures shown during the technical presentations.

## 3. TRIAL STANDARD DISTRIBUTION

The following elements are planned to be included by the co-ordinator:

- PAN standard purification by HPLC.
- Calibration of the standard by IC/Ac<sup>-</sup>.
- Dilution and addition of internal standard NPN.
- Calibration of the resulting standards by IC/Ac<sup>-</sup>.
- Distribution of standards to the participants.
- After return of control samples from the participants, the co-ordinator will analyse all by IC/Ac<sup>-</sup>.
- Additional experiments to investigate the reliability of acetate standards.

Most participants will analyse the standards with IC/Ac<sup>-</sup> immediately after reception and before return of control samples. More detailed lists of the experiments planned by the respective participants are given in enclosure 2.

Enclosure 3 contains short descriptions of some of the methods that will be used by the participants. Also refer to the phase PREP.I report.

#### **4. PAN TRANSPORT FORMALITIES**

PAN standards are potentially dangerous when transported by air. Great care has been taken to handle correctly all formalities regarding dangerous goods and customs regulations. Both the formalities and the practical aspects of PAN standard transport have been described as a method. This is included as enclosure 4.

#### **5. PAN STANDARD QUALITY CONTROL**

The intercalibration project relies on accurate documentation of all details that may affect the integrity of the PAN standards. The logging of such details has been described as a method. The first version of this method is given in enclosure 5.

A log sheet is enclosed with each standard bottle that is distributed. The participants should take care to update this log sheet every time the bottle has been moved to a new storage temperature (always -20°C or colder), has been outside the freezer some seconds, or has been opened. The bottles should only be handled using gloves, to minimize heat transfer from the fingers. All other incidents that may affect the standard, should also be noted on the sheet. Date, time and signature/initials should be added to all entries.

#### **6. ACKNOWLEDGEMENTS**

The work is financially supported by the Commission of European Communities under the contract EV4V-CT90-0222. Furthermore each participant is receiving financial support for the project from the respective governments and/or research institutions.

**ENCLOSURE 1**

**STRATEGY MEETING**





STEP PAN INTERCALIBRATION, EV4V-CT90-0222  
STRATEGY MEETING 3-5 SEPTEMBER 1991

PROJECT PLAN / WORK SCHEDULE:

- Phase PREP.II is prolonged with three weeks. The work schedule section covering project week 5-17 is changed to 5-20.
- All later events are postponed approximately three weeks.
- The coordinator will adjust the work schedule according to the above decisions, and to avoid conflict with holidays.
- Dates will be used in the work schedule in addition to calendar week numbers.
- All standard transports will be performed in the beginning of a week, so that eventual delays will not be aggravated by week-ends.
- The trial distribution will take place from NILU on Monday 14 October. The return shipments will take place on Monday 18 November 1991. (CNSA may be delayed).
- Phase CAL.I will not be started until the participants have had time to read the report from PREP.III (the trial distribution). To avoid conflict with the Christmas holiday, the CAL.I standard distribution will probably take place in the end of January 1992.
- A new project meeting will be scheduled after phase CAL.I.

CO-ORDINATOR'S NOTE:

The work schedule is a central document that all participants must read carefully. It lists the activities that each participant is bound to perform under the CEC contract. Each participant should work according to the schedule even without reminders from the co-ordinator. Where the work schedule is not clear enough, please ask the co-ordinator.

A report has been produced in phase PREP.I, and the scheduled time for phase PREP.II is running out. However the goals of both these phases have not yet been fulfilled. PREP.I should include the description of the methods currently used by each participant, in a more detailed form than in normal publications, and with emphasis on error sources. PREP.II should include method refinements through experiments based on the documentation from PREP.I.

Presently we have not produced any documentation from phase PREP.II. The co-ordinator feels that the best we can do, is to extend our current method descriptions to include descriptions of possible error sources. (The co-ordinator will try to reduce the size of his method descriptions.)

Such a set of method descriptions + the individual lists of experiments planned for phase PREP.III, will give a reasonable documentation from PREP.II. With this realistic amount of work we will be able to defend our progress according to the project contract.

TRIAL STANDARD DISTRIBUTION:

- 4 calibrations will be made of all standard bottles. Before distribution, upon receipt, before return and after return.

- Ion chromatography by the acetate method has been defined as the reference method in the project contract. The participants will in some cases use other methods, as required. If possible, some participants will use more than one method.
- The default pack will contain the following standards (approximate concentrations):
  - 8 ml: 100 µg PAN/ml + 100 µg NPN/ml
  - 8 ml: 100 µg PAN/ml
  - 8 ml: 10 µg PAN/ml + 10 µg NPN/ml
  - 8 ml: 10 µg PAN/ml
  - 8 ml: 100 µg NPN/ml
- Each participant will prepare a short list of experiments and calibrations planned to be included in the PREP.III phase (the trial standard distribution). Also special requirements for standard concentrations will be specified here.
- NILU will arrange all the transports under one contract with Aircontact Cargo in Oslo. The cost will be shared between the participants and deducted from the next payment from the CEC.
- The shadow partners that want to receive standards, will be asked to submit the same list of intended experiments. They will receive the standards free of charge, but will be asked to share the transport costs on the same basis as the other participants.

#### CALIBRATION METHOD LIBRARY:

The method library was first suggested by the co-ordinator in the internal work document from phase PREP.I. At the meeting a ring binder with 4 method descriptions from the coordinator was given to each participant. Several questions regarding the format and use of the method library and the methods had been presented in the invitation, and were discussed:

- The participants agreed that a method library is a necessary tool for the execution of the intercalibration project.
- The proposed library format and division in sections was accepted by the group.
- The format (sections, lay-out, etc.) for the method descriptions used by the coordinator was not commented, but several participants found the descriptions too detailed and too large. It was commented that it would not be possible to read so detailed descriptions from each participant. The co-ordinator pointed out that many PAN calibration errors may be caused by small practical details in the procedures, and that such details should be documented.
- It was agreed that the participants will submit method descriptions in the format and size of their own preference, with description of error sources included. Excessive detail should be avoided. Preliminary descriptions of the methods expected to be used in phase PREP.III, will be included in the phase PREP.II report.

#### TRANSPORT / CUSTOMS FORMALITIES:

Transport and customs formalities for the PAN standard transports were discussed. PAN standards will be defined as "flammable liquid". Neither the toxicity nor the oxidizing properties of pure PAN will be significant in the dilute standards that will

be transported. The method description for PAN standard transports (I910831TK) is presently being revised. The latest edition of the IATA Dangerous Goods Regulations gives additional information, but this should not lead to new conclusions. The method has a list of documents that will be prepared by the shipper. If additional documents or information is needed by the customs authorities, the participants in the respective countries must inform the co-ordinator about this.

The following points were made during the discussion:

- A copy of the Air Waybill should be sent by fax to the participants when the shipment is dispatched.
- The specified value of the standards should be set as low as possible. This is realistic, since the standards have no commercial value. The bottles, solvent and packing have an approximate value of 25 ECU.
- It will be stated in the proforma invoice that the standards are samples for scientific use, that they have no commercial value, and that they are distributed free of charge.
- The shipments should be made in the beginning of a week, to avoid additional delays due to week-ends.
- Both sender and receiver must have a representative that is ready to answer eventual questions from air lines or customs authorities during the transport.

#### MEASUREMENT PERIOD:

The meeting decided that the 1 year ambient PAN measurement period should start on 10 January 1992. The participants should generally try to start their instruments in the selected site as soon as possible. (The site should not be too far from the laboratory, as this would make the calibration experiments too time consuming and complicated.)

#### SCIENTIFIC PRESENTATIONS:

During the second day of the meeting 8 presentations of approximately 15 minutes duration were given. The material presented gave more detailed information about some of the methods and experiments described in phase PREP.I.

Rudolph, J.	KFA Jülich	What are the reasons for uncertainties of PAN measurements in the atmosphere?
Thysse	TNO	PAN measurement and calibration in the STEP project.
Toupance, G.	Univ. Paris XII	PAN analytical system used at Creteil.
Oyola, P	ARD	Status report for PAN intercalibration at ARD, Sweden.
Glavas, S.	Univ. Patras	Use of capillary columns for the analysis of PAN.
Libert, Y.	ISPRA	Continuous PAN Measurements, Operating Conditions, Calibration Techniques at J.R.C. ISPRA.

Ciccioli, P	C.N.R.	PAN and photochemical oxidants in the Tiber Valley.
Krognes, T.	NILU	PAN measurement and calibration technique used at NILU.

No formal abstracts have been prepared from these presentations. Some photocopies of presentation foils were distributed to the participants during the meeting. Copies of this material will also be included in the next internal report.

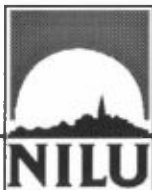
#### TECHNICAL DISCUSSIONS:

Several aspects of PAN calibration and measurement techniques were discussed after the presentations. Some of the points discussed are summed up below:

- The quality of commercial column packing materials has varied very much over the years. When a material has been found of acceptable quality, there is no way to know if the next batch of the same material from the same supplier will be acceptable. The support Chromosorb W is suspected to be more adsorptive now than it was before 1986-1987.
- The amount of water vapour in sample and carrier gas may strongly affect the adsorption problems. TNO routinely uses moist carrier gas. Most of the other participants have so far used dry carrier gas due to better detector sensitivity.
- Dr. Glavas has demonstrated that capillary columns may be used successfully for PAN measurements. No comparison so far exists between capillary columns and packed columns that are of proven high quality.
- NILU is presently constructing a new version of the ECD controller electronic module. This will be used to test baseline stability when a constant zero potential is maintained at the detector center electrode also during the detection of a chromatographic peak.
- Almost all the participants reported sloping baselines as one of the main problems of the PAN measurement technique. Carrier gas flow or pressure transients, contamination, humidity, and centre electrode potential variations are in some combination expected to be responsible for the problem.

PROGRAM  
FOR THE  
TRIAL  
PAN STANDARD  
DISTRIBUTION

STEP PAN INTERCALIBRATION  
CONTRACT EV4V-CT90-0222



The raw PAN solution was produced by the Risö laboratory in Denmark 20 March 1987. The concentration is in the range of 2000 µg PAN/ml n-heptane.

Approximately 30 ml of the raw solution will be purified on HPLC at NILU, to produce approximately 50 ml of pure PAN solution. The expected concentration of the purified solution is approximately 1000 µg PAN/ml n-hexane. This standard will be calibrated by ion chromatography at NILU.

Two dilutions will be prepared from the calibrated solution. Both will have n-propyl nitrate (NPN) added as an internal standard.



Approximately 300 ml of standard will be made with concentration close to 100  $\mu\text{g}$  PAN/ml + 100  $\mu\text{g}$  NPN/ml.

Some of the above standard will be diluted 1:10 to produce approximately 300 ml of standard with concentration close to 10  $\mu\text{g}$  PAN/ml + 10  $\mu\text{g}$  NPN/ml.

Both the two diluted standards will be calibrated by ion chromatography at NILU.





Each participating laboratory will receive 2 bottles (of 8 ml each) of each of the two dilutions.

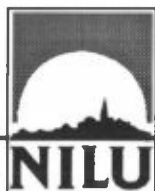
Upon special request one bottle with approximately 4 ml of the concentrated purified solution may be added to some laboratories.

**NILU**

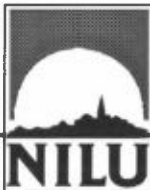
Each laboratory may store one bottle of each dilution as a backup. In this case the backup bottles should not be opened.

Laboratories that plan a more extensive experimental program, and will need both bottles of a dilution, should calibrate both bottles separately by ion chromatography.

One calibration of a standard by ion chromatography requires approximately 0,8 ml of the standard. For each bottle that will not be stored as a backup, the following program should be performed (also include local PAN standards, if available, in all experiments):



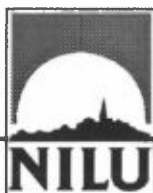
1. Calibrate the standard by ion chromatography.
2. Perform GC calibrations with the calibrated standards.
3. Perform quality control experiments to reduce uncertainty in the methods used, and attempt to quantify all error sources.
4. After a period of approximately 5 weeks, recalibrate the standards by ion chromatography.
5. Return the bottles to NILU packed with carbon ice, with a minimum of 2 ml remaining in each bottle.



Each participant should make a list of the experiments planned and return this to NILU as part of the material in phase PREP.II.

Some associated partners have not yet stated in writing the extent of the co-operation they are planning. Standards will be distributed to those that have submitted the list mentioned above.

The coordinator will arrange all the air freight of PAN standards under one contract. The participants are asked to cover equal shares of the total transport cost (approximately 1800 ECU pr participant).





**ENCLOSURE 2**

**TEST PROGRAMS FOR TRIAL DISTRIBUTION**



STEP-PAN INTERCALIBRATION program

PHASE PREP III: TRIAL TESTS  
Program of work.

G. TOUPANCE, Université Paris XII, Av. Gén. de Gaulle, 94000 CRETEL, France  
Septembre 1991

Liquid NILU samples will be analysed through alkaline hydrolysis and subsequent determination of nitrite ion concentration by IC and by Saltzman technique. GC-ECD will have been previously calibrated by IR (Créteil technique) and the response of the GC to injections of NILU samples will be tested.

1- Analysis by IC:

1.1- Solution 1 (100 $\mu$ g/ml) : 0.5ml of solution 1 and 4 ml of 0.01N sodium hydroxyde are introduced in a 10ml calibrated flask. After hydrolysis, flask is filled up to 10ml by phtalic acid to drop pH to 5-6. 100 l is injected for IC. This operation is repeated 3 times. In parallel, 1ml of solution 1 is diluted by hexane up to 10ml (Solution 1bis). This solution is used for injection in the GC, as well pure or further diluted.

1.2- Solution 2 (10 $\mu$ g/ml) : Idem as 1-1 for hydrolysis and IC analysis. Solution 2 is used for injection in the GC, as well pure or further diluted. The same operation will be done with solution 1bis, in order to test if dilution of solution 1 give results coherent with solution 2. If yes, this will indicate that circulation of concentrated solutions of PAN is sufficient for all experiments. Operator will only have to dilute conveniently the sample depending on his calibration technique.

1.3- solutions containing NPN : same tests.



2- Analysis by Saltzman technique : we would like to cross results from IC with those from Saltzman technique which every labs can use rapidly anywhere a classical UV spectrometrer is available during 1 hour. ). We propose to make the following experiments :

2.1- Solution 1 (100 $\mu$ g/ml) : 0.5ml of solution 1 and 4 ml of 0.01N sodium hydroxyde are introduced in a 10ml calibrated flask. After hydrolysis, flask is filled up to 10ml by Saltzman reactive and the UV absorption is recorded. This operation is repeated 3 times.

2.2- Solution 2 (10 $\mu$ g/ml) : Idem as 2-1 for hydrolysis and UV absorption measurement. The same operation will be done with solution lbis, in order to test again if dilution of solution 1 give results coherent with solution 2.

2.3- solutions containing NPN : same tests.

3- Calibrations : In all cases, calibration is made by standard solutions of nitrite which are analysed following the same procedures as for PAN solutions.

4- Return of solutions : If initial samples are 8ml volume, at least 2ml of each solution will be returned to NILU.

UNIVERSITY OF PATRAS  
Dr. S. Glavas

1. Determination of the half life of PAN in the glass chamber, in order to assist in the evaluation in part of the error due to the thermal decay of PAN before hydrolysis.

2. Determination of  $\text{NO}_2^-$  in a liquid PAN standard according to a procedure similar to the one described by the coordinator for the acetate analysis.

3. Determination of acetate anions in standard solutions so that we may also apply the acetate analysis as proposed by the coordinator for the determination of PAN. This method has not been used by our laboratory because we cannot HPLC purify our liquid PAN standards and we therefore measure too large concentrations of acetate anions, due to the acetic or peracetic acid from the preparation of the PAN.

4. (Co-ordinator's addition) Determination of PAN standard concentration by glass chamber dilution followed by alkaline hydrolysis and  $\text{NO}_2^-$  analysis by ion chromatography.

5. (Co-ordinator's addition) Repetition of the PAN standard calibration before return of control samples to the co-ordinator.

Dr. J. C. Th. Hollander

From: IMW-TNO  
To: NILU  
Date: october, 15, 1991

Experiments planned in PREP III phase: Trial Intercalibration

A. Synthesis of a fresh PAN in octane solution.

Target concentration about 1000  $\mu\text{g}/\text{ml}$ .

The sample is only purified by repeated washings with ice-water, no HPLC purification is applied.

The sample will be divided in at least two portions, one of which will serve as a back-up.

B. TNO will receive from NILU two bottles (of 8 ml each) of each of two dilutions of PAN in heptane.

It is understood that these samples have been purified by HPLC.

The preferred target concentrations are:

lower level of about 100-200  $\mu\text{g}/\text{ml}$

higher level of about 500-700  $\mu\text{g}/\text{ml}$

Both samples WITHOUT internal standard (propyl nitrate).

The addition of a blank heptane sample would be appreciated.

Each second bottle will serve as a back-up.

C. First analyses round.

In the first week after arrival of the samples all samples (including back-up samples) will be analysed by:

1. FTIR of liquid phase:

three aliquotes of each sample and octane and heptane blanks taking into account IR-peaks at 787, 1153 and 1294  $\text{cm}^{-1}$ .

2. IC-analyses of the hydrolyses products Ac and  $\text{NO}_2/\text{NO}_3$  from three aliquots of each sample in duplicate.

The analyses include proper analytical standards and blanks.

D. GC-ECD analyses at permanent monitoring site.

In the second or third week after arrival of the samples three samples (not back-ups) are taken to the monitoring site.

Based on each liquid standard three gaseous concentrations will be made by static dilution which will be analysed in triplicate by GC-ECD.

The concentrations in the gaseous phase will be in the range of 0.5 to 4 ppb of PAN where linearity and precision of the GC-method are good.

E. Second analyses round.

In the fourth week the samples used for GC analyses which have been transported to and from the monitoring site will be analysed as in paragraph C.

In case of large discrepancies with the first assessment, the back-up samples will also be analysed again.

**Experiments Planed in Trial Calibration Exercise.**

1. All samples (NILU samples and dilutions of them) will be kept at -20 °C.
2. Aliquots of 0.1 cm<sup>3</sup> will be used for further experiments.
3. Immediately after withdrawal from the NILU-sample, a 1/100 diluted solution in cold (-20 °C) Hexan will be prepared (secondary sample).
4. Two "column" and two "loop" analyses of 0.001 cm<sup>3</sup> will be performed for each secondary sample.
5. A tertiary sample will be prepared by dilution of the secondary sample if the ECD response of the secondary sample is > 10<sup>7</sup> integration area units.
6. Two "column" and two "loop" analyses will be made for each tertiary sample.
7. Additionally analyses of Hexan will be performed ("zero PAN" sample).  
For preparation of diluted solution a 0.1 cm<sup>3</sup> Eppendorff pipette and 100 cm<sup>3</sup> quoted glass flask will be used. A home-made glass injector and 0.100 cm<sup>3</sup> Hamilton 700 syringe will be used for injections at room temperature (+21 °C).

C.N.R., ITALY  
Dr. P. Ciccioli

EXPERIMENTS PLANNED ON THE DISTRIBUTED SAMPLES

The sample received from NILU will be certified in the following way:

- 1) aliquots will be dissolved in a alkaline solution
- 2) the hydrolyzed sample will be analyzed for its content of nitrite by ion chromatography (three times).
- 3) the signal will be checked by GC and the response factors with respect to propylnitrate evaluated.
- 4) repeated analysis will be carried out before sending the sample back to NILU.

JRC ISPRA, ITALY  
Y. Libert

PROGRAMM OF EXPERIMENTS FOR PAN PREP.III  
(Trial standard distribution)

- A Determination of the amount of PAN in standards at the arrival:
- Ionic chromatography
  - Spectrocolorimetry (Saltzman)
  - Cathodic stripping voltammetry
- B Calibration test of the G.C.
- Ventilation of a liquid standard
  - Injection of a liquid standard
  - Injection of a gas standard
- C Determination of the amount of PAN in standards before sending them back to NILU

We have no specific requirement to make about standard. We agree with those defined in strategy meeting at the beginning of the month.

## **Planned measurements for trial distribution**

### *1. Analysts of PAN solutions*

Small volumes of the PAN solutions (between 0.1 and 1 ml) will be hydrolysed in 5 or 10 ml of 0.05 N sodium hydroxide. The alkaline solutions will be analysed by a **modified** Griess-Saltzman method for nitrite. Nitrate will also be analyzed in several samples to check for impurities. We plan also to analyse for acetate ions, however our quite old "organic ion" IC has had a complete breakdown in the electronics and although the DIONEX service has twice tried a repair it, it is still not running at all. We will probably have the samples analysed elsewhere.

### *2. Comparison with our PAN solutions and the permeation source*

The PAN solution will be diluted with hexane to concentrations suitable for direct GC-injections. These dilutions will be compared with similar solutions prepared from our PAN solutions.

Furthermore the solutions will be compared to GC-measurements of our calibration gas.

AEA, HARWELL, UNITED KINGDOM  
Dr. G. Dollard

(Co-ordinator's addition) Dr. Dollard intends to calibrate the standards using nitrite analysis (ion chromatography) and possibly nitrate analysis via a Saltzmann type reaction. The calibrations should be made twice; after distribution and before return of control samples to the co-ordinator.





**ENCLOSURE 3**

**CALIBRATION METHOD DESCRIPTIONS**



## STEP-PAN INTERCALIBRATION program

### Calibration of PAN analysers at créteil by gas IR spectrometry and static dilution

G. TOUPANCE, Université Paris XII, Av. Gén. de Gaulle, 94000 CRETEL, France  
Septembre 1991

Principle of the method : Pure PAN is introduced in an IR gas cell and the concentration is measured from IR absorptions bands of PAN (100-300ppm). This mixture is then diluted (factor 6856) by static dilution. The final mixture is in the range 15-50 ppb. GC-ECD PAN analyser is calibrated by syringe injection of 0.1-1 ml of the diluted mixture.

1- Preparation of PAN : PAN is prepared by classical nitration of peracetic acid and is extracted in dodecane. This solvent is used for IR calibration because its low vapor pressure allows further recovery of gaseous PAN with good purity. From this point of view tridecane is better but so expensive that it must be reserved to experiments where no trace of solvent is strictly needed. For routine calibration of PAN analysers dodecane is excellent. PAN solution is kept in freeze at  $-20^{\circ}\text{C}$ .

2- Transfer of PAN into the IR gas cell : A flask of 50 ml of freezed solution of PAN in dodecane is connected to a vacuum line and air is evacuated. Then, solution is gently warmed up by immersion in liquid water at room temperature. During the melting of cristals, PAN is desorbed and moves to the gas phase. Gaseous PAN is then tranfered to the IR cell (10cm path, 150 ml volume) by connecting the flask to the cell previously evacuated to vacuum. Concentration of PAN in the cell ranges usually from 50 to 200 ppm, depending on experimental conditions and PAN concentration in dodecane solution.

3- IR spectrum : IR cell is stayed 10mn before recording spectrum. This is to wait the initial decrease of PAN due to absorption on walls. The IR spectrum is recorded on a Fourier 1710 Perkin Elmer spectrometer, using the base line and water vapor substraction facilities. Time  $t_1$  of obtention of the spectrum is noted. Concentration of PAN is calculated from the absorption of 3 different bands, using the most recent determinations of absorption coefficients (Tsalkani and Toupance, 1990).

4- Dilution : The dilution device is made of a 0.326 ml calibrated pyrex volume which can be connected to the IR cell and to a 2l pyrex flask (2235 ml exactly) equiped with a septum and a rotating teflon agitator (static dilution by a factor 6856). Vacuum is made in the system and then the calibrated volume is connected to the IR cell. Operation is repeted 3 times to assure quantitative filling of the calibrated volume. The PAN aliquot is then transferred to the 2l flask by connecting the calibrated volume to the flask. Diluted mixture is achieved by addition of pure  $\text{N}_2$  up to 1 atmosphere and slow agitation. This first preparation of a diluted mixture

assures the saturation of the walls of the whole device by PAN. This phase is strictly necessary for a good reproductibility of the calibration. Erratic results are obtained if such carefull equilibration of the system with PAN is not achieved because PAN losses on walls. The system is then pumped again and a second dilution is performed : calibrated volume filled 3 times from PAN in the IR cell, etc... The moment when PAN is transfered from the calibrated volume to the 2l flask is noted as time  $t_2$ . At that time it is considered that the concentration obtained in the 2l flask can be strictly derived by a factor 6856 from the concentration of PAN in the IR cell at that moment.

5- Injection on the GC-ECD : after 5 mn of agitation, the content of the 2l flask is considered to be homogeneous. 0.1 to 1 ml samples (syringe) are taken (septum) and injected into the GC. For each sample volume injected, the response of GC is plotted as a function of time. For a correctly conditioned column, the signal decreases slowly with time. For each volume sample, virtual signal at the moment of preparation of the diluted mixture is calculated by extrapolation at time  $t_2$  .

6- Calibration : During phase 5, the IR cell is installed again in the IR spectrometer and a second spectrum is recorded at time  $t_3$ . Concentration in the cell at the moment  $t_2$  when dilution was made, is calculated by interpolation between  $t_1$  and  $t_3$ . This value is used to calculate the diluted concentration into the 2l flask at time  $t_2$  and then to derive the calibration curve of the GC. In field operation conditions, the volume of the sample loop we use is 4ml. So, an injection of 0.1 ml of synthetic diluted mixture in the range 15-50 ppb corresponds to 0.3 to 1 ppb of PAN in the 4ml natural sample.

7- Remarks : in spite of numerous possible causes of errors, this procedure has given very coherent results with other techniques, as calibration with PAN samples in hexane directly injected into the GC and calibrated by analysis of  $\text{NO}_2^-$  ions, as well from ion chromatography as from Saltzman method.

STEP-PAN INTERCALIBRATION program

Calibration of PAN analysers at Créteil by  
alkaline hydrolysis and nitrite ions determination.

G. TOUPANCE, Université Paris XII, Av. Gén. de Gaulle, 94000 CRETEL, France  
Septembre 1991

1- Preparation of PAN solutions : PAN is prepared by the classical technique of nitration of peracetic acid. PAN is extracted in hexane, a volatile solvent which allows direct injection into the GC-ECD. Solution is divided into samples of some ml which are kept in freezer at  $-20^{\circ}\text{C}$ . For calibration one tube is taken from the freezer (solution 1).

2- Preparation of solution for injection into the GC-ECD : An aliquot of solution 1 is diluted by hexane to 1/20000, through successive operations in calibrated flasks (solution 2). 0.1 to  $1\mu\text{l}$  of this solution 2 is injected into the GC and the response plotted as a function of sample volume.

3- Determination of the concentration of PAN in solution 1 :

3.1- by Saltzman technique : 0.5 ml of solution 1 (conveniently diluted previously if necessary) and 4ml of 0.01N sodium hydroxyde are introduced in a 10ml calibrated flask. After hydrolysis the volume is filled up to 10 ml by Saltzman reactive. Concentration of nitrite ions is determined by UV absorption of the solution.

3.2- by IC of  $\text{NO}_2^-$  ions : 0.5 ml of solution 1 (conveniently diluted previously if necessary) and 4ml of 0.01N sodium hydroxyde are introduced in a 10ml calibrated flask. After hydrolysis the volume is filled up to 10 ml by phtalic acid 0.004M to drop pH to 5-6. Solution is then analysed by IC : injection  $100\mu\text{l}$ , VYDAC 302IC column, eluant phtalate buffer pH 4.5, conductimetric detection.

4- Calibration : In both cases, calibration is made by using standard solutions of nitrite ions which are analysed following the same procedure as for PAN solutions.



# DETERMINATION OF PAN STANDARD CONCENTRATION

Sotirios Glavas

Department of Chemistry, University of Patras, GR-26110 Patras, Hellas.

Based on  $\text{NO}_2^-$  measurement.

The method currently employed in our laboratory for the determination of a gaseous PAN standard, depends on the conversion of PAN to  $\text{NO}_2^-$  by alkaline hydrolysis and subsequent analysis of  $\text{NO}_2^-$  by ion chromatography.



It is known that some  $\text{NO}_2^-$  is oxidised to  $\text{NO}_3^-$ . The chemical equation for this conversion is uncertain.

## PROCEDURE

1. Preparation of gaseous PAN mixture and conversion of PAN to  $\text{NO}_2^-$ .

One ml of the liquid PAN standard (containing 100  $\mu\text{g}$  or 10  $\mu\text{g}$  PAN/ml) will be introduced into our glass chamber of volume 425 L filled with purified air. The resulting PAN mixture will be either  $\approx 40$  or  $\approx 4$  ppbv PAN, IF there is no PAN destruction in the transfer line or the chamber's walls. Subsequently a gaseous sample will be drawn through an impinger, used for the analysis of ozone in the standard methods of analysis of air pollutants,



containing 10 ml of 25 mM sodium hydroxide, at a flow rate of 100 ml/min for a time period sufficiently long to obtain a good  $\text{NO}_2^-$  peak on the ion chromatograph. (20-50 min)

## 2. Determination of $\text{NO}_2^-$ .

Aliquots of the solution resulting from the hydrolysis of PAN in the impinger are diluted 1:5 with eluant consisting of 1.8 mM  $\text{NaHCO}_3$  and 1.7 mM  $\text{Na}_2\text{CO}_3$ . Using a sample loop of 100  $\mu\text{l}$  three samples will be introduced into the Dionex 4500 ion chromatograph provided with a conductivity detector. The  $\text{NO}_2^-$  and  $\text{NO}_3^-$  will be separated on a Dionex AS4A column using as precolumn the Dionex AG4A. With an eluan flow rate of 2 ml/min the  $\text{NO}_2^-$  ions elute in 1.8 minutes and the  $\text{NO}_3^-$  in 3.2 minutes.

## 3. Calibration of the ion chromatograph for $\text{NO}_2^-$ .

Depending on the concentration of  $\text{NO}_2^-$  that results from the "unknown" PAN standard we use five  $\text{NO}_2^-$  standards of such concentration as to encircle the determined  $\text{NO}_2^-$  concentration of the unknown. The  $\text{NO}_2^-$  standards are prepared by appropriate dilutions of a concentrated  $\text{NO}_2^-$  solution containing 1 g pro analysi grade  $\text{NaNO}_2$  per liter of Milli-Q water. A similar procedure will be followed for the analysis and calibration of the ion chromatograph for the  $\text{NO}_3^-$  using  $\text{NaNO}_3$  solutions.

## 4. Calculations.

From the volume of the gaseous PAN standard that passed through the impinger and the measurement of the peak height of  $\text{NO}_2^-$ , which is known from the calibration of the ion chromatograph to correspond to a certain amount of  $\text{NO}_2^-$ , we com-

pute the amount of PAN standard. To the amount of PAN that results from the measurement of  $\text{NO}_2^-$  we include the amount of the measured  $\text{NO}_3^-$  (without multiplication by three).

#### 5. Error sources.

The major error source in this procedure is expected to be due to the thermal decay of PAN during its introduction in the smog chamber as well as during its residence in the 425 L chamber.

In addition to the above unquantified error, additional random errors may be attributed to the standard practices of a chemical laboratory such as weighing errors, impurities of  $\text{NaNO}_2$  and  $\text{NaNO}_3$ , volumetric errors etc. Furthermore an additional error may be attributed to the stoichiometry between  $\text{NO}_2^-$  and  $\text{NO}_3^-$  produced during the alkaline hydrolysis of PAN.



Dr. J. C. Th. Hollander

Mr. Terje Krognæs

NILU

Lillestrøm

Norway

Dear Terje,

I have prepared a short list of the experiments planned for the PREP II phase.

The list also specifies the requirements for the standards to be distributed.

I also prepared a summary of the main error sources of the analytical methods which will be applied. In particular this summary shows how we intend to identify and quantify these error sources from the results of the trial intercalibration experiments.

At present I am not able to present detailed method descriptions on the IC- and FTIR-analysis.

On the former I have yet not received any details from our analytical department. With the latter we have more experience, but not in written detailed form.

Any preliminary attempt at present to produce a method description would be a waste of time and only result in crude statements.

We do intend to have the methods worked out in standard operating procedures. I can probably supply these with the results of the trial intercomparison.

The GC-method has been described in detail in the PREP-I report. The FTIR there in general terms.

From: IMW-TNO  
To: NILU  
Date: october, 15, 1991

#### Main Error Sources

- A. Loss of sample integrity during transport and provisional storage can be an important source of bias in the analytical results. Such losses can be assessed by repeated analyses at strategic intervals, taking into account the various phases in the sample routing. Thus, the samples are analysed at NILU before shipment to TNO, shortly after arrival at TNO, shortly before return to NILU and after arrival at NILU. Just in the middle of this route is the transport of the samples from the TNO laboratories to the monitoring site and back. Loss of sample integrity during this excursion is assessed by omitting the back-up samples from it. Comparison of the back-up samples with those taken to the monitoring site will reveal an eventual problem.
- B. Bias in analytical methods to assess the concentration of PAN in the liquid standards can be identified and probably quantified by comparison of the results of different analytical methods, which will have different biases. FTIR analyses requires no sample treatment. The samples are measured as obtained. Quantification relies on specific absorptivities taken from literature and any bias in those will be transferred to the analytical results. An other source of bias are impurities ( residues of peroxy acetic acid, acetate and nitrate ) resulting from the synthesis or decay during storage. The measurement of three different IR bands on both HPLC purified and only ice-water washed samples will give a clue to bias due to impurities. IC analyses of acetate and nitrite/nitrate ions after hydrolyses of the PAN solutions can be biased by systematic low hydrolyses efficiencies. Impurities in the samples (see above) may also in this method contribute to the bias. The acetate to nitrite/nitrate ratio in the purified and not purified solutions will give clues on the latter contributions to bias. The GC-ECD analyses is most specific for PAN analyses. No bias is expected in this method. It is, however, noted that quantification of PAN by this method is not absolute; it relies on very similar standards as assessed in the intercalibration experiment. This degrades the GC method to only a relative comparison of the concentrations in the samples, but by a bias free very precise method.

C. Precision errors will differ for different methods. On the one hand they will be due to the intrinsic properties of for example detectors in the analytical equipment used, on the other hand they will depend on the sample treatment steps in the complete analytical method. With FTIR the sample is analysed without any treatment. Precision is mainly related to establishing proper baselines for and integration of the IR bands and temperature differences between samples and between samples and blanks. The aggregated precision error is simply derived from repeated analyses of multiplicate aliquots.

With IC analyses there are two main contributions to the precision error. First, there is the precision of the analytical method itself- which is derived from the analyses of the analytical standards and blanks.

Additional contributions result from variability in the hydrolyses efficiency, volumetric errors in the hydrolyses routine and sample decay in the analytical process. The latter contributions will show up in an aggregated way as an increase in the precision error in the analyses of hydrolysed PAN samples as compared to the analyses of analytical standards.

The GC analyses also has two main contributions to the precision error. The analytical performance of the gas chromatographic system with respect to precision is mainly determined by chromatographic performance, detector performance, establishing the baseline of the PAN peak and the integration of the peak. This is determined from multiple measurements on a single gaseous sample. The second main contribution results from the production of static dilutions on basis of the liquid samples. These are mainly volumetric errors related to the volume of air and the volume of the PAN aliquote injected in it. There may also be a contribution from decay of PAN during preparation of the mixture and its subsequent analyses. The latter can be assessed from an analyses of a time series of analyses, the former from the increase of the precision error of a series of measurements of independant static dilutions as compared with the precision obtained in the measurement of a single static dilution.

As a first step it may be sufficient to identify and quantify the main contributions to the bias and precision errors in an aggregated form. When unexpected high and impracticable contributions are observed, these may be investigated in more detail. It has, however, to be recognized that in some cases it will be very difficult to disentangle the various contributions.



## Technical Details of the PAN-Calibration Procedure.

P. Matuska, MeteoConsult GmbH, Germany

The following procedure of the PAN-calibration is applied at the baseline station Izana/Canary Islands:

A glass flask (Pyrex, 1000 cm<sup>3</sup>) containing a Penray mercury lamp (254 nm line) is used for preparing the gaseous PAN-calibration mixture. The flask is equipped with two Teflon valves for gas inlet and outlet, one Teflon valve for the connection of the pressure gauge, one septum holder with septum for injection of acetone and withdrawal of gas mixture and the Penray holder. The flask is evacuated to ca. 1 - 3 hPa by means of a rotary pump and filled with NO<sub>2</sub>/synthetic air mixture to ca. 1100 hPa. This operation is repeated three times. To this mixture 0.015 cm<sup>3</sup> acetone is added using a Hamilton 700 syringe. After 20 min equilibration time the photolysis is started. The photolysis time is 4 min. The flask is located in an air conditioned room at a temperature of 21 °C. Aliquots of 0.100 cm<sup>3</sup> of the photolysis mixture are injected (PS series C syringe) in the column (downstream of the - 83°C preconcentration loop) or in the loop. Injections are performed at 10 min, 1 h, 2 h, 3 h and 4 h after the end of the photolysis. At each time two "column" and one "loop" injections are made in intervals of 5 min between them. To calculate the calibration factor, we use the values of the three analyses at 10 min after the end of photolysis, the 80% NO<sub>2</sub>-to-PAN conversion rate and the TECAN determined NO<sub>2</sub>-concentration.

### Possible Error Sources.

1. NO<sub>2</sub> concentration determined by TECAN device.
2. NO<sub>2</sub>-to-PAN conversion rate. We use a conversion rate of 80%, but it is known that the rate depends on surface nature of the reaction vessel. It is possible that the surface changes its quality with time. We use the same flask since 1989. At



present we have no possibilities to determinate the conversion rate e.g. Ion Chromatography.

3. Non-linearity of the ECD-response. We use the response of the calibration PAN amount of  $10^6$  integration area units to evaluate unknown PAN concentrations with responses ranging over  $5 \cdot 10^2$  -  $10^6$  integration area units. We do not use all values of the calibration procedure for testing the ECD response because already the calculated PAN concentrations for different decay times can fluctuate by about 40%.

PROJECT STEP : PAN INTERCALIBRATION  
(Contract N° EV4V- CT90-0222)

METHOD PROPOSED BY CNR-IIA FOR THE CALIBRATION OF PAN ANALYZERS

Prepared by : P. Ciccioli, M. Possanzini, A. Cecinato, V. Di Palo, E. Brancaleoni and A. Brachetti.

PRINCIPLE OF THE METHOD

PAN is produced at ppb levels by irradiating with a U.V. light (Mercury lamp) mixtures of acetaldehyde and  $\text{NO}_2$  dynamically generated by permeation tubes. Formation takes place through the same chain of reactions occurring in the atmosphere. To make possible the quantification of PAN in the gas mixture by alkaline hydrolysis and liquid ion chromatography carried out on the nitrite ion, possible interfering components (  $\text{NO}_2$ ,  $\text{HNO}_3$  and ozone) are removed at the outlet of the photochemical reactor by using an assembly of annular denuders set in series. The first denuder is coated with eugenol for the removal of ozone whereas the second is coated with eugenol+ $\text{NaOH}$  that retains quantitatively  $\text{NO}_2$  and  $\text{HNO}_3$ . The amount of PAN produced by the system can be modulated by reducing the intensity of the U.V. lamp, by changing the permeation rates of reagents or by further dilution with air or nitrogen. Under steady state conditions, the amount of PAN released by the system is constant for many hours so that it is possible to quantify the GC signal by looking at the nitrate ion formed in a alkaline solution placed at the outlet of the sampling valve. Flow rates from 0.1 to 1 L/min can be used without problems. The system is suitable for calibrations of PAN at ppb-ppt levels in the field.

#### INSTRUMENTATION REQUIRED

- a) Permeation device comprised of permeation tubes for NO<sub>2</sub> and acetaldehyde and a thermostatic bath for controlling the temperature in the range between 25 and 45°C.
- b) Photochemical flow reactor equipped with a Hg lamp and a shutter for regulating the light intensity.
- c) Two glass annular denuders (20 cm in length with a 0.3 distance between the annulus).
- d) Solutions in Methanol of Eugenol and Eugenol+ NaOH.
- e) A bottle of air with relative humidity ranging between 20 and 50%.
- f) A microimpinger.
- g) Alkaline solutions.
- h) A liquid ion chromatograph with suppression systems for the quantitation of nitrite ions at low levels.
- i) Teflon lines with Swagelok connectors.

#### LIMITATIONS

The only limitation of the method is related to the capacity of the denuder system that must be replaced if calibrations requiring more than 4 hours collection time are undertaken.

ACETATE ANALYSIS FOR PAN STANDARD CALIBRATION  
OPERATING CONDITIONS AT ISPRA

Y. Libert

We used for comments your method of numeration

3 CHEMICALS

- Eluent: Mother solution 12,5 mM. A dilution of 1/10 gives eluent to 1,25 mM. Dilutions are made in Millipore water.
- Regenerating agent for the suppressor 0,025 M H<sub>2</sub>SO<sub>4</sub>
- Acetate Standard solution: 1000 ppm (Mother). Dilutions are used.
- With high matrix solutions in NaOH filter are used for injection of standard and sample : "Dionex OnGuard<sup>TM</sup>-H cartridges". We now make hydrolysis in 0,033 M NaOH .

4 EQUIPMENT

- Dionex 2010i Chromatograph
- Dionex HPIC-AG4 Guard Column
- Dionex HPIC-AS4 25 cm Column
- Dionex Micro Membrane Suppressor Type AMMS-1
- 50 µl Sample loop.
- Peristaltic pump for eluent , suppressor agent and sample.
- Integrator Spectra-Physics "Data Jet".
- Eppendorf Pipettes. 1ml-100µl , 10-100 µl.

5 PROCEDURE

Idem till to 5-5.

5-5 Diluted eluent, 1,25 mM, is degassed by void.

5-6 Without object

5-7 Without object

5-8 Start of the ion chromatograph:

Idem except the following:

-Sample loop 50  $\mu$ l

-Suppressor regenerating agent flow 2ml/min.

-Detector sensitivity : 1-3-10  $\mu$ S

-After stabilisation the following normal conditions should be observed:

Pressure(after the eluent pump)  $\approx$  950 psi

Baseline conductivity, approximately 3,4  $\mu$ S

.....

5-12 Sequence of operation

We first inject "mother eluent" after that millipore water after this run we inject 3 standards and proceed with sample analysis, three to four samples, and then newly 3 standards.

## 7 ERROR SOURCE AND ACCURACY

We have also find that the peak heights increeases with continuous operations

### TOTAL ERROR BUDGET

It seems to be in the order of 10%.

ADSORPTIVE VOLTAMMETRIC DETERMINATION OF  $\text{NO}_2^-$  IN WATER SAMPLES  
APPLICATION TO PAN MEASUREMENTS OF SOLUTION AFTER SODA HYDROLYSIS

Summary This bulletin describes the voltammetric determination of nitrite in water samples up to a concentration of 2 ppb. The nitrite is first derivatized by diazotation with sulfanilamide, followed by coupling to 1-naphtylamide to produce an azo dye which is enriched at the HMDE (Hanging Mercury Drop Electrode). The following determination employs DPCSV (Differential Pulse Cathodic Stripping Voltammetry).

Instruments

646 VA Processor with 647 VA Stand of Metrohm

Reagents

- N-(1-Naphtyl)-ethylendiamin-dihydrochlorid (MERK)
- Sulfanilamid (MERK)
- Boric acid (MERK)
- NaOH titrisol (MERK)
- $\text{NO}_2\text{Na}$  (MERK)
- HCl suprapur (MERK)

Ready prepared solutions

- N-(1-Naphtyl)-Ethylendiamin-dihydrochlorid 0,01 M ; 0,05 M HCl
- Sulfanilamide 0,2 M ; 0,7 M HCl
- NaOH 1M
- Buffer Solution : 1 M Boric acid & 0,5 M NaOH
- Standard solution: Mother: 1g/l  $\text{NO}_2^-$  prepared from  $\text{NO}_2\text{Na}$  which has been dried for 1 h at 110°C.

Daughter : 10 ppm  $\text{NO}_2^-$

## Procedure

A 10 ml aliquot of the sample is pipetted into the voltammetric cell. 100  $\mu$ l of Sulfanilamide solution is added giving a pH of 2,5. The solution is then mixed and after approximately 1 min. 100  $\mu$ l of Naphtylamine solution is added. Full development of the Azo compound takes ca 5 min. After this 40  $\mu$ l of the 1 M Sodium Hydroxyde is added and then 100  $\mu$ l of the borate pH buffer, giving a final pH of ca. 8,4. The solution is deaerated by bubbling  $N_2$  gas for 4 min.

The Voltammogram is recorded as follow :

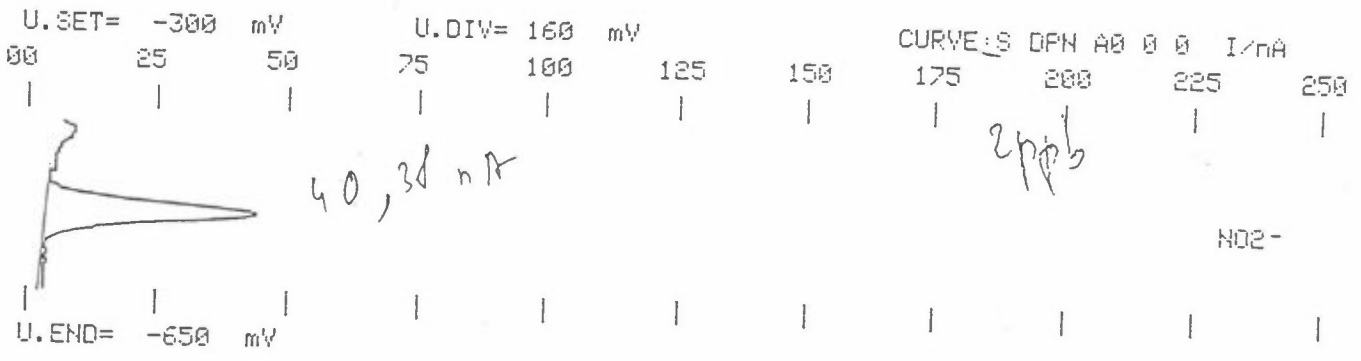
- Electrode/drop size	HMDE/5
- U set (enrichment)	-300 mv
- U Stop	-650 mv
-Electrolysis with stirring	60 s
-Electrolysis without stirring	10 s
- Method/amplitude	DP/-50 mv
- $t$ drop	0,2 s
- Sweep rate	20 mv/s
- Reduction peak of the Azo	-480 mv

## Remarks

- The pH value of the final solution must be checked for the correct adherence to the exact value in each case, it may be possible to have to adjust after addition of buffer (pH=8,4  $\pm$ 0,1).
- In these conditions the blank of the reagents is in the order of 0,4 ppb . It can be lowered for low concentrations of  $NO_2^-$  inferior to 1 ppb by reducing the amount of reagents in this case a control of linearity must be made.

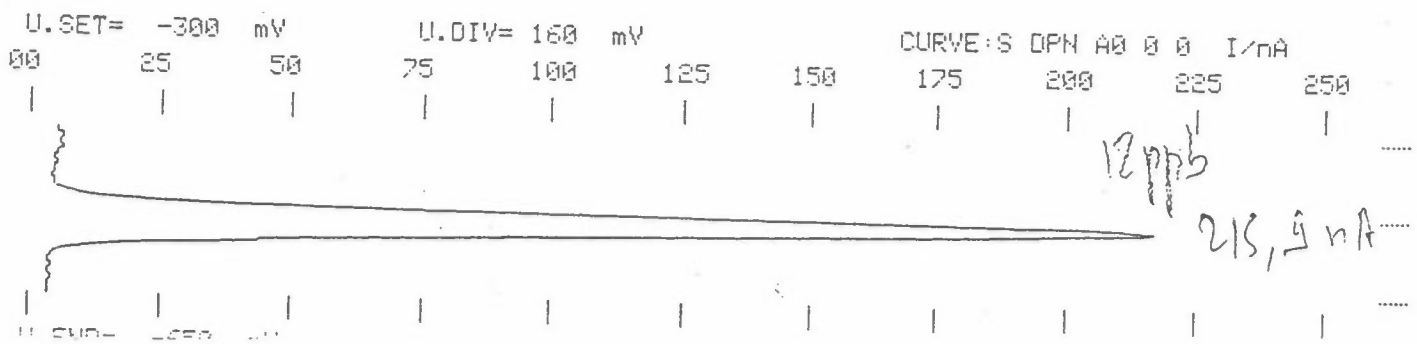
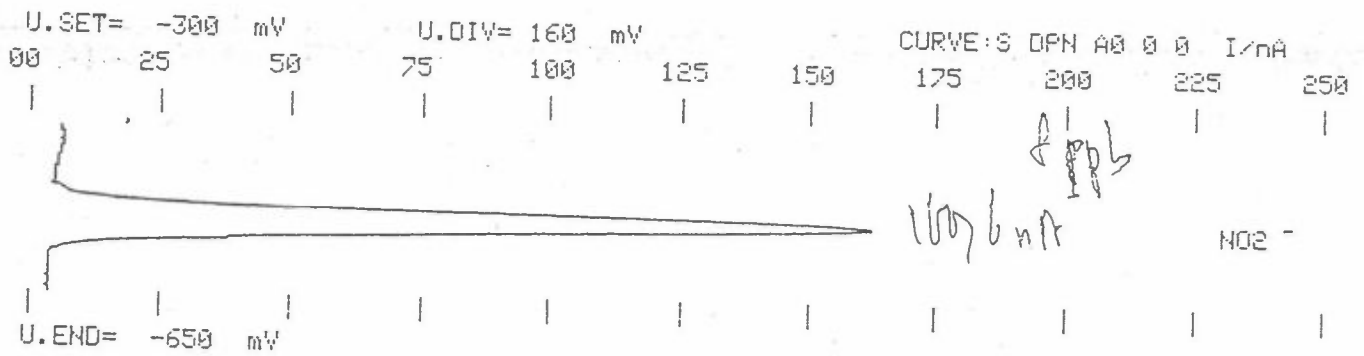
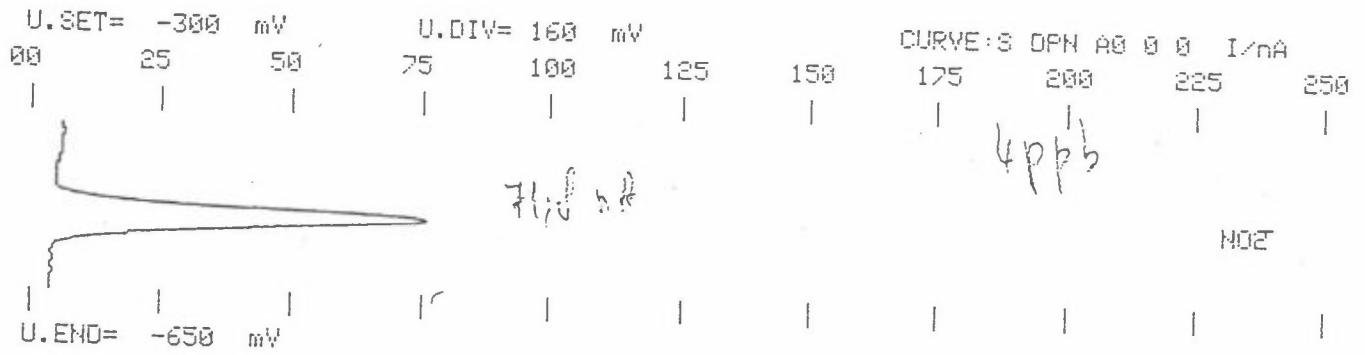
## Reference

Constant M.G., Van den Berg and Hong Li  
The determination of nanomolar level of Nitrite in fresh and sea water by cathodic stripping voltammetry  
Anal.Chim.Acta 218 (1988) 31-41



CALIBRATION FOR NO2<sup>-</sup> BY Cathodic Stripping Voltammetry

Fig. VI







## DETERMINATION OF P A N

### *1. Permeation system*

In a thermostatted glass vessel a solution of peroxyacetyl nitrate (PAN) in heptan is placed. A purified gas flows through a PTFE tube immersed into the solution with a constant flow rate of  $50 \text{ cm}^3 \text{ min}^{-1}$ . To improve the long term stability of the permeation source, the temperature should be kept below  $0^\circ\text{C}$ . The temperature and the concentration of the PAN solution is adjusted to obtain a PAN concentration of a few ppb in the calibration gas.

### *2. PAN analysis in the permeation gas*

For the determination of the PAN concentration, the permeation gas is bubbled for several hours through a small impinger with an internal diameter of 8 mm, a total length of 30 cm filled with 8 ml 0.05 N sodium hydroxyde solution. The hydrolysis of PAN in alkaline solutions is spontaneous and quantitative and results in one mole of nitrite ion per mole of PAN (1). The hydrolysis efficiency is occasionally checked with a second impinger of the same type.

### *3. PAN analysts in organic solutions*

Between 0.1 and 1 ml of the organic solution is added to 5 or 10 ml of 0.1 or 0.05 N aqueous sodiumhydroxide solution in a glass vessel and shaken for several minutes. The concentration and volume of the sodium hydroxide solution depends on the expected PAN concentration. If necessary the sodium hydroxide solution is further diluted prior to the analysis.

### *4. Nitrite measurements*

The nitrite ion concentration in solution is quantified by a colorimetric method (2) using a modified Griess reaction. The nitrite ion reacts with sulfanilamide under acidic conditions to form a diazo compound. This compound then couples with N-1-naphthylethylendiamine dihydrochloride to form a reddish-purple azo dye with an absorption maximum at 544 nm (3). The nitrite measurements are calibrated with solutions of potassium nitrite at different concentrations. Measurements are only made in the linear range of the calibration curve (about 3 orders of magnitude). The detection limit is 1.5 ng/ml of ni-

trite nitrogen. The reproducibility of the determination of PAN in the calibration gas is estimated to be about 5 %.

## References

- (1) Stephens, E.R., The formation of molecular oxygen by alkaline hydrolysis of peroxyacetylnitrate, *Atmosph. Environment* 1, 19-22, 1967
- (2) Grasshoff, K., *Methods of seawater analysis*, Verlag Chemie, 1976
- (3) Saltzman, B.E., Colorimetric microdetermination of nitrogen dioxide in the atmosphere, *Anal. Chem.* 26, pp 1949, 1954

## Instrument:

Technicon Auto-Analyzer II and a  
Perkin-Elmer Spektrophotometer 551  
with a 20 mm path length flow cell.

Solutions	Flowrates (ml/min)
Sample	0,8
Ammoniumchloride, 11 g/l	2.0
Reaction solution: (Sulfanilamide, 20 g n-Naphthylethyldiamine, 1 g and o-Phosphoric acid, 100 ml in 1l solution)	0.23

**ENCLOSURE 4**

**TRANSPORT OF PAN IN LIQUID SOLUTION**



# TRANSPORT OF PAN IN LIQUID SOLUTION

Terje Krognes  
NILU (Norwegian Institute for Air Research)

## 1. INTRODUCTION

PAN (Peroxyacetyl Nitrate) is thermally unstable, and is stored at  $-20^{\circ}\text{C}$  diluted in a solvent. During transport it should always be kept at the same or a lower temperature. Only a few minutes at a higher temperature is enough to destroy the standard (partial decomposition of PAN changes the concentration of the standard).

Carbon ice is used to freeze PAN standards during transport. Consequently three separate dangerous goods are involved; PAN (toxic, oxidizing substance), the solvent (flammable liquid), and carbon ice. The dilution is sufficient to remove any possibility of exothermic decomposition. Temperature control is not required to prevent exothermic reactions. However, freezing is required to maintain the exact, calibrated concentration of the standards.

When PAN standards are transported, an unforeseen delay may lead to depletion of the carbon ice. The PAN standards will then be heated above  $-20^{\circ}\text{C}$  and the calibration will be invalidated. Careful planning of all transport and customs formalities is therefore an important part of the transport procedure. This document will be presented to the air-freight company before PAN standards are distributed in the STEP PAN intercalibration project (contract EV4V-CT90-0222).

## 2. THEORETICAL BACKGROUND

### 2.1. PURE PAN

PAN is an organic peroxide, containing the bivalent -O-O- structure. It is covered by the definition of Division 5.2 in section 3.5.1 in the IATA DANGEROUS GOODS REGULATIONS (1991) (later referred to as DGR). Pure PAN is explosive and toxic, and would not be allowed in an airplane. For the same reason pure PAN is avoided in most experimental work.

The chemical formula of PAN is  $\text{CH}_3\text{-C(=O)-O-O-NO}_2$ . The molecular weight of PAN is 105. The available oxygen content of pure PAN is 15,2% (DGR section 3.5.4 Note 1).

The inhalation toxicity of pure PAN (4-hour LC<sub>50</sub>) is 96 ppm for rats (Verschueren, 1983). This corresponds to a 1-hour LC<sub>50</sub> of 192 (DGR section 3.6.4). The maximum limit for packing group I is set to 1000 ml/m<sup>3</sup> (=1000 ppm). This places pure PAN in packing group I when toxicity is regarded. Saturated vapour concentration and vapour pressure data are not available for PAN.

## 2.2. LIQUID SOLUTION PAN STANDARDS

PAN calibration standards are dissolved in a solvent (normally pentane, hexane or nonane). Raw solutions prepared during PAN synthesis may contain in the order of 10 mg PAN/ml. Purified PAN solutions for calibration use normally contain from 1 µg PAN/ml to 1 mg PAN/ml. The lightest of the diluents, pentane, has a density of 0,621 g/cm<sup>3</sup>. Any PAN standard solution offered for transport will thus contain less than 0,25% available oxygen. The solution falls outside the definition of division 5.2 (DGR section 3.5.4(a) and 3.5.4(b)), and is not considered dangerous under class 5.

Also the toxicity is reduced in the diluted PAN standards. The solvent itself is not classified as toxic. Section 3.6.5(a)(1) of the DGR specifies that the toxicity of the mixture is found by dividing the PAN LC<sub>50</sub> with the mole fraction of PAN in the mixture. The worst case will now be a solution of 10 mg PAN/ml nonane. The mole fraction of PAN in this mixture is approximately 0,017. The LC<sub>50</sub> of the mixture is consequently larger than 11000. The PAN solution falls outside the definition of a toxic substance when inhalation toxicity is considered (section 3.6.2 of the DGR).

The only remaining hazards are those of the solvent (flammable liquid) and of the carbon ice used in the packing.

## 2.3. INTERNAL STANDARD N-PROPYL NITRATE (UN1865)

An internal standard is added to some of the PAN standards that are offered for transport. This internal standard is n-propyl nitrate, which is a flammable liquid in packing group II. It is added in the same small concentrations as PAN, and it does not introduce any subsidiary risk, and the flash point of n-propyl nitrate is higher than for the solvent normally used. For these reasons n-propyl nitrate is not declared separately in the Shipper's Declaration of dangerous goods.

## 2.4. DANGEROUS GOODS IN EXCEPTED QUANTITIES

The amounts of PAN standards in liquid solution that are to be transported, are small enough to be defined as excepted quantities (DGR section 1.7.6). Each

standard bottle contains 30 ml or less of a flammable liquid (class 3, packing group I or II). The total amount of flammable liquid in one outer packing is 300 ml or less. Also the conditions of DGR section 1.7.6(b) are met.

The carbon ice needed to maintain the calibrated concentration of the PAN standards, is classified in class 9, packing group III. The amount needed in one pack is approximately 12 kg. This is not within the excepted quantity limit of 1 kg. The pack is therefore not permitted under the excepted quantity rules. Furthermore, carbon ice is not allowed under the limited quantity regulations (DGR section 1.7.7).

## 2.5. APPLICABLE PACKING INSTRUCTIONS

The different solvents used in PAN standards fall into different UN packing groups, and are covered by different packing instructions (valid for passenger aircraft) as shown in the table below (also the internal standard and the carbon ice are included in the table):

Name	UN No	Class	Label	UN Pkg Group	Pkg instr.	Max net qty	Flash point
n-Pentane	UN1265	3	Flammable liquid	I	302	1L	-49°C
Hexanes	UN1208	3	Flammable liquid	II	305 Y305	5L 1L	-23°C
Heptanes	UN1206	3	Flammable liquid	II	305 Y305	5L 1L	-4°C
Nonanes	UN1920	3	Flammable liquid	III	309 Y309	60L 10L	31°C
n-Propyl nitrate	UN1865	3	Flammable liquid	II	305 Y305	5L 1L	23°C
Carbon dioxide, solid [Dry ice]	UN1845	9	Miscellaneous	III	904	200kg	

The flash points listed in the table above are given in the Janssen Chimica catalogue (1988). Even if some of the solvents used for PAN solutions are listed in packing group II or III, it is convenient to use routinely for all PAN standard transports a packing which is suitable for both packing group I substances (packing instruction 302) and packing group II substances (packing instruction 305). In addition to the general rules, certain operator variations apply. According to the variations listed in packing instruction 302, class 3 flammable liquids in packing group I will not be allowed by Indian Airlines, Trans World Airlines or Tunis Air. The same limitations apply to packing instruction 305. Furthermore, Delta



Airlines, Eastern Airlines, United Airlines and Air Wisconsin do not accept hexanes for transport (packing instruction 305).

The PAN standard transports will use a quadruple packing with glass sample vials as inner packing. A cushioned tin can (1/3 litre paint box type) is the second packing. This will be packed in carbon ice and enclosed in a cardboard box lined with 7 cm of styrofoam on all 6 sides (not gas tight). The cardboard box fits inside a 6mm UN/ICAO-certified plywood box (specification 4D, DGR section 6.1.19). The plywood box is a Nefab Vikex 40577 FG with external dimensions 400\*400\*400 mm. The inner packings conform to the texts in DGR section 6.1.1 (IP.1) and 6.1.3 (IP.3). These sections do not specify any tests, and no special tests have been performed on the inner packings.

## **2.6. CARBON ICE**

The carbon ice used for freezing the PAN standards is placed in class 9 (miscellaneous dangerous goods). It is not considered very dangerous in the small quantities involved here (approximately 12 kg per package), provided the packing is designed to release the carbon dioxide gas so that ruptures are prevented. When carbon ice is transported by a qualified freight agent, it does not create any problems. When carbon ice is carried by a passenger as checked baggage or carry-on baggage, confusion may arise due to operator variations. Normally 2 kg of carbon ice is allowed in carry-on baggage.

The carbon ice is delivered in solid blocks or in pellets. Pellets have larger surface area, giving larger freezing capacity and shorter lifetime if the insulation is poor. The best result is obtained with a mixture of solid chunks and crushed carbon ice. The crushed ice has a very large surface area, providing large freezing capacity during load peaks. The chunks ensure that some freezing capacity will be retained for a maximum amount of time. The mixture of chunks and crushed carbon ice is easily packed around the inner box to ensure efficient freezing.

## **3. CHEMICALS**

- Carbon ice block.

## **4. EQUIPMENT**

- UN/ICAO-certified outer box (NEFAB 40577 FG)
- Cardboard box internally lined with styrofoam (Norsk Hydro, Oslo).
- 0,33 litre tin can with paper padding for the standard bottles.

- 8 ml glass sample vials (Brown 153002) with teflon lined screw corks (Brown 150932).
- (A hard plastic camping bag with extra styrofoam lining may be used as carry-on luggage if agreement from the airline is given in advance.)

## **5. PROCEDURE**

### **5.1. PREPARING THE TRANSPORT BOX**

The NEFAB plywood box is delivered flat-packed in one piece. It is erected and the bottom is fixed in place by hammering flat the four metal tabs. Norsk Hydro in Oslo delivers carbon ice in a cardboard box with an internal styrofoam box that holds 40 kg (approximately 27 litres) of carbon ice in solid blocks. The styrofoam box is lined with an additional 5 cm layer of styrofoam on all six sides (see drawings in enclosure 1). The internal volume should now be approximately 9,2 litres. This volume accomodates approximately 12 kg of solid carbon ice.

A 0,3 litre tin can is filled with suitable cushions (paper tissues) for the bottles to be transported. The cushioning material must be capable of absorbing all the liquid if the bottles should be broken. The bottles should be held firmly in place inside the tin can when the lid is closed.

### **5.2. PAN STANDARD DOCUMENTS**

When the bottles were filled, they were given unique names, and a log sheet was created for each bottle. Before the packing, note the time and date of the packing and the destination of the transport that will take place. Make a photo copy of the entire log sheet (including the log sheets of any parental standards) and store this in your own binder. The original should be sendt with the bottles in the transport.

### **5.3. TRANSPORT AND CUSTOMS DOCUMENTS**

The following documents should be prepared by the shipper (the person/company that is responsible for truthfully declaring the contents of the shipment):

- Proforma invoice in two signed copies
- Shipper's declaration for dangerous goods in two signed copies
- EUR-1 declaration (see below)

The PAN standards have no commercial value. The bottles and packing have a value of approximately 10 ECU. In most cases no export customs declaration is

needed. If an import customs declaration is needed, this will be written by the freight agent in the destination country, based on the information given in the proforma invoice.

The EUR-1 declaration serves to identify the country of origin of the goods. It is normally required by Spain and Italy, among others. Most other European countries accept instead that a statement is included in the proforma invoice:

I, the undersigned, exporter of the goods covered by this document, declare that the goods meet the conditions required to obtain originating status in preferential trade with the EEC and that the country of origin of the goods is Norway.

The statement above will be included in all invoices. For parcels being shipped to Italy and Spain, also a EUR.1 certificate will be issued. Copies of all documents should be mailed to the recipient for reference, and to help him with the completion of similar documents for the return transport (if any). Examples of the above documents are given in enclosure 2. A copy of the air waybill will be telefaxed to the recipient from the sender's freight agent when the transport is dispatched.

#### **5.4. TRANSPORT BOX LABELLING**

The following labels are required on the box:

- Address label with complete institutional address, and with complete name and telephone number of contact person at the recipient's address.
- Label identifying the shipper, with complete institutional address and name and telephone number of his contact person.
- IATA/ICAO hazard label for dangerous goods class 3 (flammable liquid).
- IATA/ICAO handling labels to indicate correct orientation of the box (up/down)

Examples of the above labels are given in enclosure 3.

#### **5.5. TRANSPORT AGREEMENT**

A description of the chemical properties of PAN (in a terminology acceptable to the air lines), the recipient's address and telephone/telefax numbers, and all transport documents should be forwarded to the freight agent a week before the transport will take place. The packing is designed to retain the carbon ice for at

least four days, but a door to door delivery within 48 hours should be agreed. Also the recipient must agree to the date of the transport, and be available during the transport in case of any complications. He should provide information of his preferred local freight agent, contact persons and telephone/telefax numbers, preferrably at least two weeks before the transport.

#### **5.6. PAN STANDARD PACKING**

Approximately two hours before the pack will be picked up by the freight agent, put the tin can and cushioning material in the freezer. The can and cushioning should be at -20°C or lower when the standards are packed approximately one hour later. Check that the bottle corks are firmly closed. The bottles should be packed quickly to avoid heating them. Secure the lid on the tin can and place the packed can in the freezer.

When working with carbon ice, always wear insulating gloves. Fill the outer box approximately 1/4 with a mixture of large carbon ice chunks and crushed carbon ice. Remove the packed tin can from the freezer and place it in the outer box. Immediately fill the outer box to the top of the inner insulation with a mixture of large carbon ice chunks and crushed carbon ice. Position the styrofoam insulation in the top of the box. Place an envelope with the PAN standard log sheets on top of the insulation and close the outer box. The four metal tabs are carefully hammered flat to secure the lid. Do not use excessive force, as this may destroy the tabs and prevent re-use of the box.

#### **5.7. PAN STANDARD UNPACKING**

Immediately after receipt of the pack, the box should be inspected and opened. The four metal tabs on the lid are carefully lifted with a screw driver and straightened. The lid may now be opened. Store the box and all inner packings for re-use in the return transport.

Note on the log sheets for all bottles in the transport the date and time of arrival, the amount of carbon ice left, and whether the carbon ice is properly packed around all surfaces of the tin can. Using insulating gloves, remove the carbon ice on the top, open the tin can with a screw driver and quickly transfer the standard bottles to the freezer. Insert the updated log sheets in your binder.

## **5.8. RETURN OF CONTROL SAMPLES**

The packing material and boxes should be re-used for the return transport. Examples of proforma invoice, shipper's declaration for dangerous goods, and address labels will be issued from the co-ordinator. The documents may be signed and used by the participants, or they may issue new documents. The EUR.1 certificate is not needed for import in Norway.

Approximately 2 ml of each standard should be returned in the original bottle, using the same procedures as described above.

## **6. CALCULATIONS**

## **7. ERROR SOURCES AND ACCURACY**

Depletion of the carbon ice may result if the transport is unexpectedly delayed. 48-hour service from door to door should be included in the agreement with the freight carrier. The carbon ice in the pack should normally last 4-5 days. If the carbon ice is depleted, the PAN standard is immediately destroyed. Even if the temperature only for a short time has been above  $-20^{\circ}\text{C}$ , the standard will be partially decomposed, and the calibration is no longer valid.

If a block of carbon ice is used, the temperature within the pack may not be uniform. If the tin can is resting on top of the carbon ice block for a prolonged time without being enclosed in carbon ice, the effective storage temperature may very easily rise above  $-20^{\circ}\text{C}$ . If the tin can after the transport is not found to be properly enclosed in carbon ice, the effective storage temperature during transport must be defined as unknown, and the calibration of the standards is no longer valid.

## **8. REFERENCES**

DANGEROUS GOODS REGULATIONS, 32d edition (1991) IATA  
(International Air Travel Association)

JANSSEN CHIMICA, Catalogue/Handbook of Fine Chemicals, 1988, Janssen  
Pharmaceutica, B-2340 Beerse, Belgium

Verschueren, K. (1983) Handbook of Environmental Data on Organic Chemicals.  
2.ed. N. Y., Van Nostrand, 965-968





**ENCLOSURE 1**

**DRAWINGS OF TRANSPORT BOX  
AND INNER TIN CAN**



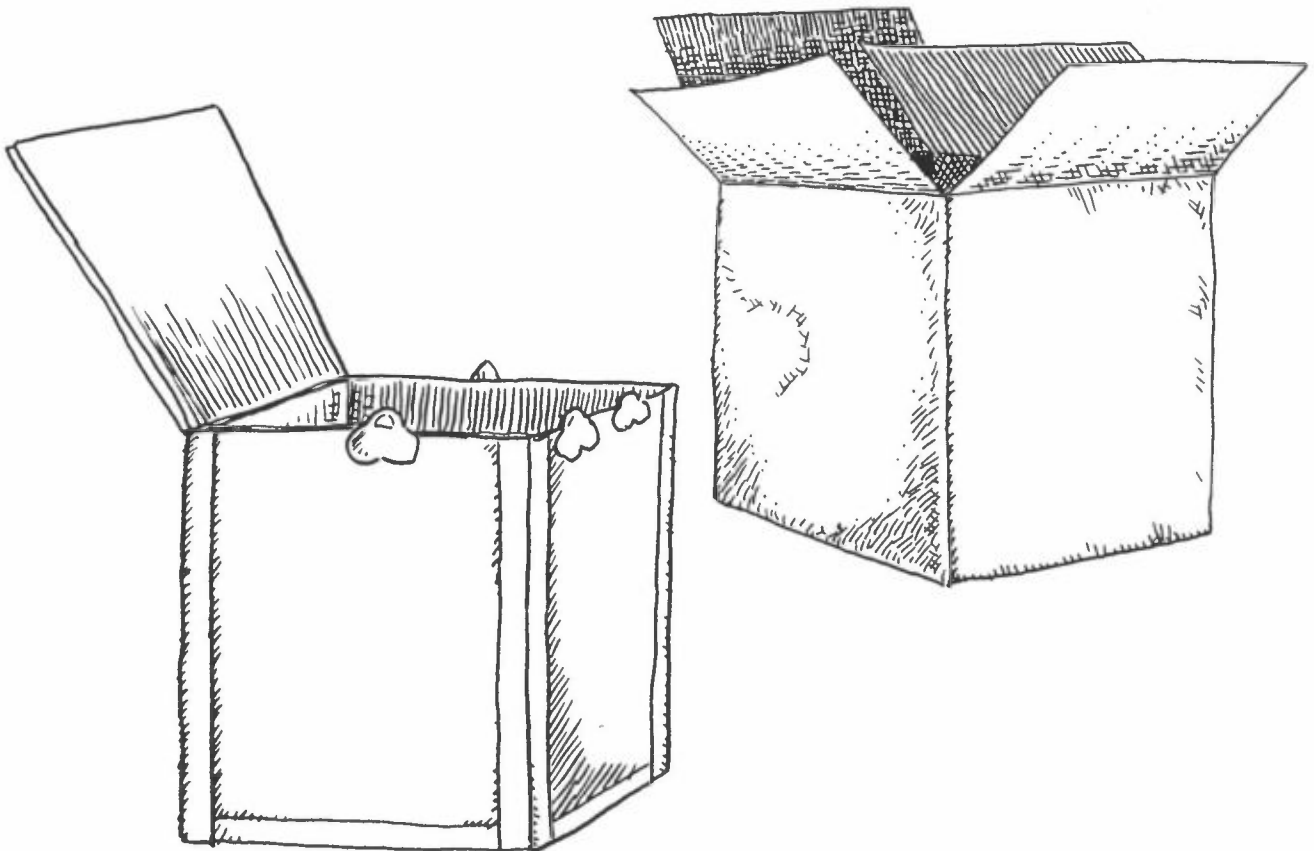
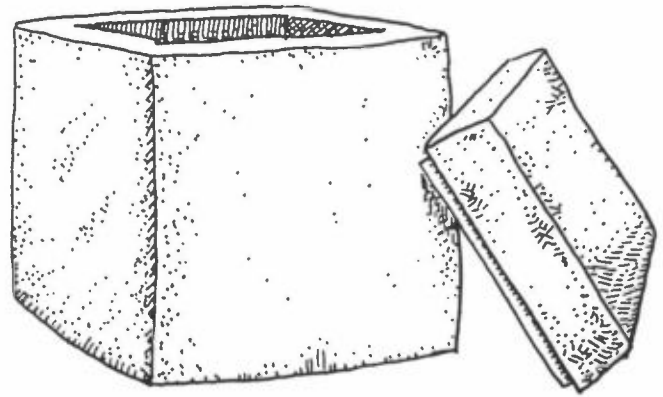




Glass bottles wrapped in paper and enclosed in tin can with lid.

Tin can packed with approximately 12 kg of carbon ice in a 70 mm styrofoam box.

Styrofoam box enclosed in cardboard box, and packed in UN/ICAO-certified plywood box.





**ENCLOSURE 2**

**EXAMPLES OF TRANSPORT  
AND CUSTOMS DOCUMENTS**

**TRANSPORT OF PAN IN LIQUID SOLUTION**



NORSK INSTITUTT FOR LUFTFORSKNING - NORWEGIAN INSTITUTE FOR AIR RESEARCH

POSTBOKS 64 - N-2001 LILLESTRØM - NORGE



Instituto de Salud Carlos III  
 Centro Nacional de Sanidad Ambiental  
 Area de Contaminacion Atmosferica  
 28220 MAJADAHONDA  
 SPAIN

Your ref.: Dr. R. F. Patier      Our ref.: TK/WS/O-91052      Lillestrøm, 21 oktober 1991

PROFORMA INVOICE

5 bottles of PAN (Peroxyacetyl nitrate) and NPN (n-propyl nitrate) calibration standards diluted in hexane with the following approximate concentrations and volumes:

1 bottle	8 mL	100 µg PAN/mL + 100 µg NPN/mL
1 bottle	8 mL	100 µg PAN/mL
1 bottle	8 mL	10 µg PAN/mL + 10 µg NPN/mL
1 bottle	8 mL	10 µg PAN/mL
1 bottle	8 mL	100 µg NPN/mL

The standards are used for intercalibration experiments to improve measurements of air pollution. They are only used for scientific purposes. They have no commercial value. They are delivered free of charge. The value of the bottles and packing material is approximately 100 NOK ( = 12 ECU ).

NORSK INSTITUTT FOR LUFTFORSKNING

*Wenche Solheim*  
 Wenche Solheim

I, the undersigned, exporter of the goods covered by this document, declare that the goods meet the conditions required to obtain originating status in preferential trade with the EEC and that the country of origin of the goods is Norway.

*Wenche Solheim*, 21.10.91  
*Wenche Solheim*  
 NILU Wenche Solheim

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

Postal address:  
 P.O.Box 64  
 N-2001 LILLESTRØM, Norway

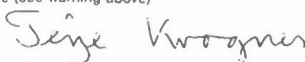
Office address:  
 Elvegt. 52  
 LILLESTRØM

Telephone: (06) 81 41 70  
 Telefax : (06) 81 92 47  
 Telex : 74854 nilu n

Bank: 5102.05.19030  
 Postgiro: 0813 3308327

TRANSPORT OF PAN IN LIQUID SOLUTION

Shipper's Declaration for Dangerous Goods

Shipper NORWEGIAN INSTITUTE FOR AIR RESEARCH Elvegaten 52 2000 Lillestrøm NORWAY				Air Waybill No.  Page 1 of 1 Pages  Shipper's Reference Number							
Consignee Instituto de Salud Carlos III Centro Nacional de Sanidad Ambiental Area de Contaminacion Atmosferica 28220 MAJADAHONDA SPAIN											
Two completed and signed copies of this Declaration must be handed to the operator				WARNING  Failure to comply in all respects with the applicable Dangerous Goods Regulations may be in breach of the applicable law, subject to legal penalties. This Declaration must not, in any circumstances, be completed and/or signed by a consolidator, a forwarder or an IATA cargo agent.							
TRANSPORT DETAILS  This shipment is within the limitations prescribed for (delete non-applicable)								Airport of Departure  OSLO			
PASSENGER AND CARGO AIRCRAFT	<del>XXXXXX</del> <del>CARGO AIRCRAFT</del> <del>ONLY</del>							Shipment type (delete non-applicable) NON-RADIOACTIVE <del>RADIOACTIVE</del>			
Airport of Destination: MADRID											
NATURE AND QUANTITY OF DANGEROUS GOODS (see sub-Section 8.1 of IATA Dangerous Goods Regulations)											
Dangerous Goods Identification											
Proper Shipping Name		Class or Division	UN or ID No.	Subsidiary risk	Quantity and type of packing	Packing Inst.	Authorization				
Hexane		3	UN1208		40 mL	305,II					
Carbon dioxide, solid [Dry ice]		9	UN1845		12 kg  All packed in one plywood box	904,III					
Additional Handling Information  Flash point for UN1208 is -23°C.											
I hereby declare that the contents of this consignment are fully and accurately described above by proper shipping name and are classified, packed, marked and labelled, and are in all respects in the proper condition for transport by air according to the applicable International and National Government Regulations.					Name/Title of Signatory Terje Krognæs / Scientist						
					Place and Date Oslo, 16 October 1991						
					Signature (see warning above) 						

(5612)

1840b

TRANSPORT OF PAN IN LIQUID SOLUTION

## VARESERTIKAT

<b>1</b> Eksporter (navn, fullstendig adresse, land) NORWEGIAN INSTITUTE FOR AIR RESEARCH P.O. BOX 64 N-2001 LILLESTRØM NORWAY	<b>EUR. 1</b> <b>Nr. E</b> 188121	
<b>3</b> Mottaker (navn, fullstendig adresse, land) (utfylling ikke påkrevet) INSTITUTO DE SALVO CARLOS III CENTRO NACIONAL DE SANIDAD AMBIENTAL AREA DE CONTAMINACION ATMOSFERICA 28220 MAJADAHONDA SPAIN	<b>2</b> Se notene på baksiden før sertifikatet fylles ut. Varesertifikat til bruk i preferansesamhandelen mellom <b>NORGE</b> og det land, grupper av land eller territorier som er nevnt i rubrikk 5.	
<b>6</b> Opplysninger om transporten (utfylling ikke påkrevet) AIR CARGO	<b>4</b> Land, gruppe av land eller territorium hvor varene anses ha sin opprinnelse NORWAY	<b>5</b> Bestemmelsesland, -gruppe av land eller -territorier EEC
<b>8</b> Løpnr., kolloidens merke, nr., antall og art <sup>1)</sup> ; vareslag 1. ADDRESS, 1 PLYWOOD BOX, PAN STANDARDS	<b>9</b> Bruttovekt (kg) eller annet mål (l, m <sup>3</sup> , etc.) 40 mL	<b>10</b> Fakturaer (utfylling ikke påkrevet)
<b>11</b> TOLLVESENETS PÅTEGNING Erklæringen attesteres. Eksportdokument <sup>2)</sup> : Formular _____ Nr. _____ Tollsted/tollstasjon..... Utstedelsesland eller territorium: <b>NORGE</b> Dato..... _____ (Underskrift)	<b>12</b> EKSPORTØRENS ERKLÆRING Undertegnede erklærer at de ovenfor nevnte varer oppfyller de vilkår som kreves for å få utstedt dette varesertifikat. Sted og dato LILLESTRØM, 21 OCTOBER 1991 Underskrift Wenche Solheim	

1) Dersom varene ikke er emballert, oppgi antall vareenheter eller "i bulk".

2) Utfylles bare hvis lovbestemmelsene i eksportlandet eller -territoriet krever det.

TRANSPORT OF PAN IN LIQUID SOLUTION



**ERKLÆRING FRA EKSPORTØREN**

Jeg undertegnede, eksportør av varene som er beskrevet på forsiden,

**ERKLÆRER** at varene oppfyller de vilkår som er fastsatt for utstedelse av dette varesertifikat;

**BESKRIVER** med dette de forhold som har gjort det mulig for varene å oppfylle disse vilkår:

THE GOODS HAVE BEEN PRODUCED IN NORWAY  
USING PRODUCTS ORIGINATING IN EEC/EFTA.

**FREMLEGGER** følgende bevisdokumenter<sup>1)</sup>:

**FORPLIKTER MEG** til på de ansvarlige myndigheters forlangende å fremskaffe alle ytterligere bevis disse finner nødvendige for utstedelse av vedlagte sertifikat, såvel som, eventuelt, av de nevnte myndigheter å godta enhver kontroll av mitt regnskap og av forholdene i forbindelse med fremstillingen av ovennevnte varer;

**SØKER OM** utstedelse av varesertifikat for disse varer.

LILLESTRØM

den 21 OCTOBER 1991

Wenche Solheim  
(Underskrift)

Hvordan dette formularet skal brukes når det blir krevd områdetollbehandling i henhold til Artikkel 25.1 (EFTA tollsats).

Artikkel 25.1 i Vedlegg B til EFTA-konvensjonen og i Protokoll 3 i avtalene mellom EFTA landene og EØF angir de vilkår som må være oppfylt for at varer skal kunne innføres mot EFTA tollsats til EFTA landene samt til Danmark og Storbritannia. Hvis varene oppfyller disse opprinnelsesvilkår (og dessuten vilkårene for tollrestitusjon i Artikkel 23), skal følgende ord angis tydelig i rubrikken for bemerkninger på varesertifikatet: •ART. 25.1 OPPFYLT•.

<sup>1)</sup> For eksempel: importdokumenter, varesertifikater, fakturaer, erklæringer fra produsenten, etc., vedrørende materialer som er anvendt i produksjonen eller varer som reeksporteres i uendret stand.

**NOTER FOR UTFYLING AV VARESERTIFIKATET**

1. Raderinger eller rettelser ved å skrive ord oppå hverandre i varesertifikatet er ikke tillatt. Endringer må gjøres ved å stryke de uriktige og eventuelt tilføye de riktige opplysninger. Endringer foretatt på denne måten skal signeres av den som har utstedt sertifikatet og attesteres av tollmyndighetene i vedkommende land eller territorium hvor sertifikatet er utstedt.
2. Alle vareposter i sertifikatet skal føres opp uten mellomrom mellom de enkelte poster, og foran hver post skal anføres et løpenummer. Like under siste post trekkes en horisontal strek. Den ubrukte del av feltet skal overstrekkes for å gjøre enhver senere tilføyelse umulig.
3. Varene skal betegnes ifølge handelssedvane og med en nøyaktighet som gjør det mulig å kunne identifisere dem.


TRANSPORT OF PAN IN LIQUID SOLUTION

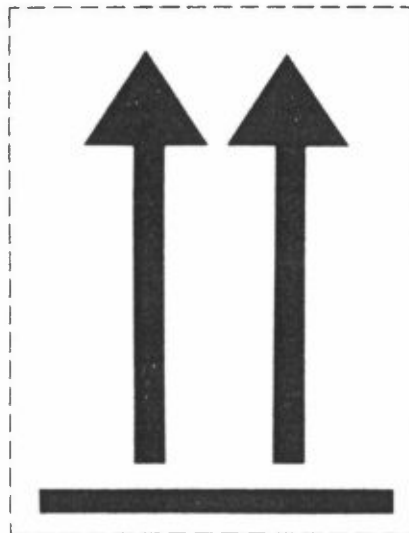
**ENCLOSURE 3**

**EXAMPLES OF LABELS  
FOR THE TRANSPORT BOX**

TRANSPORT OF PAN IN LIQUID SOLUTION



<b>DELIVER WITHIN 48 HOURS FROM DISPATCH TO:</b>	
<b>Instituto de Salud Carlos III Centro Nacional de Sanidad Ambiental Area de Contaminacion Atmospherica 28220 MAJADAHONDA SPAIN</b>	
<b>CONTACT PERSON:</b> Dr. Rosalia Fernandez Patier Tel +34 1 63 81 111 Fax +34 1 63 91 711	
	<b>SENDER:</b> NORWEGIAN INSTITUTE FOR AIR RESEARCH P.O. BOX 64 N-2001 LILLESTRØM NORWAY
<b>CONTACT PERSON:</b> Terje Krognnes Tel +476 81 41 70 Fax +476 81 92 47	



**ENCLOSURE 5**

**QUALITY CONTROL OF PAN STANDARDS**



# QUALITY CONTROL OF LIQUID SOLUTION PAN STANDARDS

Terje Krognes  
NILU (Norwegian Institute for Air Research)

## **1. INTRODUCTION**

PAN (peroxyacetyl nitrate) standards are easily destroyed by thermal decomposition, adsorptive loss, or evaporative loss. For this reason, a stable, certified PAN standard cannot be made. If unexpected results appear in a PAN instrument calibration, it is often difficult to know whether something has happened to the instrument or to the standard. To reduce uncertainties in PAN instrument calibration, it is therefore essential to keep an accurate log of what is happening to the PAN standards.

## **2. THEORETICAL BACKGROUND**

### **2.1. DEFINING A PAN STANDARD**

A primary PAN standard is one bottle, steel cylinder, bag, diffusion tube or permeation tube that contains pure PAN or PAN diluted in a liquid solvent or in a gas. Its concentration of PAN or output rate of PAN is known through at least two standard calibrations (performed before and after use of the standard), and its history is described in an accompanying log-sheet.

The primary standard should be sufficiently stable to be used for several PAN instrument calibrations over a period of at least two months (when handled and stored in accordance with the appropriate methods). More short-lived standards are called secondary PAN standards. These include dilutions that are usable for a short period (some hours or days), and are difficult to re-calibrate after use.



## 2.2. NAMING A PAN STANDARD

To allow efficient tracking of the history of a standard, each standard should be given a unique name. When part of the standard is transferred to a new bottle, this is considered a separate standard, and given a new name. When a standard is diluted in its original bottle, or an internal standard is added to it, the event must be logged. If the standard has already been used in its original form, a new name should be defined to avoid confusion.

The prefix "PAN" may be used both for Peroxyacetyl nitrate and for mixtures of different members of the homologue series. After a six digit date, the maker of the standard should use his initials followed by a serial number (if more than one bottle is prepared at the same date). For example, the standard PAN910919TK24 is bottle nr 24 prepared by TK on 19 September 1991. When a part of a standard is transferred to a new bottle, the new bottle receives a new name that automatically indicates the date of the transfer and the person that performed it. In this case also the original name should be written on the bottle label.

## 2.3. CREATING A PAN STANDARD

A new liquid solution PAN standard is created in one of the following ways:

- A solution containing PAN is made through PAN synthesis
- A new PAN solution is made through purification (preparative HPLC) of an old solution
- An old PAN solution is diluted, mixed with an internal standard (NPN, n-propyl nitrate), or mixed with another PAN standard
- A part of an old PAN solution is transferred to a new bottle

Each bottle should be accompanied by a separate log sheet that contains all relevant information of the standard. When the bottle is used, opened, transported or heated above  $-20^{\circ}\text{C}$ , the log sheet should be updated immediately. When part of a standard is transferred to a new bottle, an updated copy of the original bottle's log-sheet should be attached to the log sheet of the new bottle.

A section in the calibration method library binder is reserved for PAN standard log sheets. When a standard is transported to a new laboratory, the sender should store a copy of the log sheet and send the original with the standard. PAN standards may very easily be destroyed or partly destroyed by careless handling or mishaps. The log sheets are of major importance to the reliability of the PAN intercalibration results.

### **3. CHEMICALS**

### **4. EQUIPMENT**

### **5. PROCEDURE**

#### **5.1. CREATING THE LOG SHEET**

When a new liquid solution PAN standard is created in one of the 4 ways listed above, immediately assign a name according to the convention above. Make a photo copy of the log sheet in enclosure 1 (both pages). Complete the sections concerning bottle type, origin of the standard, and nominal concentration of the standard. Enter any special information in the last table on the first page of the log sheet. Complete the first row of the second page (bottle storage and handling) with the temperature in the freezer. Complete each entry with signature or initials.

#### **5.2. UPDATING THE LOG SHEET**

Every normal use of the standard bottle will result in one or several entries in the bottle storage and handling table. When the bottle is transferred to a new freezer, both the time (even if only a few seconds) and the new storage temperature should be noted.

When a bottle is opened, all columns (except the new storage temperature) should be completed. A transport to a different laboratory will result in two entries; one when the bottle is packed in carbon ice, and one when the bottle is unpacked in the new location.

All calibrations of the standard should be noted in the table on the first page, and in the bottle storage and handling table on the second page. Additional pages should be created as required.

Always enclose the original log sheet with the bottle when it is transported, and keep a copy in your own files.

## **6. CALCULATIONS**

If a standard is gradually deteriorating in spite of sufficiently cold storage, the PAN concentration will most probably not be reduced proportionally with storage time. The concentration may be expected to be reduced in steps every time the bottle is opened for use. Reliable data are not available for the equilibrium vapour pressure over the PAN solution. The log sheet is therefore designed to register all incidents where a standard bottle is opened. The vapour phase volume may be calculated. If a consistent loss of PAN is seen (that is not correlated to heating of the bottle), there will be sufficient information to calculate the amount of PAN that was residing in the vapour phase (and that was lost when the bottle was opened). In this way a model for calculating the changes in a PAN standard concentration may be constructed.

## **7. ERROR SOURCES AND ACCURACY**

A large number of possible error sources should be considered:

- Contamination in bottle, cork or seal
- Active surfaces in bottle or seal
- Leakage in cork/seal
- Thermal decomposition of PAN
- Loss of PAN residing in the vapour phase (when bottle is opened)
- Contamination from pipette tips
- Condensation of water vapour into the cold bottle

The quality control measures described in this method are mainly aimed at registering all incidents of temperature change and opening of the bottle. Care should be taken to always use heat insulating gloves when handling the standard bottles. Heat from unprotected fingers would be an unquantified error source in the evaporative loss calculations described above.

## **8. REFERENCES**

**ENCLOSURE 1**

**LOG SHEET**  
**FOR**  
**PAN STANDARD QUALITY CONTROL**



<b>BOTTLE NAME:</b>	<b>PAGE NO.:</b>
---------------------	------------------

## PAN STANDARD LOG SHEET

**ORIGIN OF THE STANDARD:**

	DATE / PLACE	METHOD	SOLVENT	BOTTLE NAME
SYNTHESIS				
PURIFICAT.				

**MIXED FROM OTHER BOTTLES:**

BOTTLE NAME	NOMINAL PAN CONCENTRATION <small>µg PAN/mL</small>	NOMINAL NPN CONCENTRATION <small>µg NPN/mL</small>	SOLVENT	VOLUME <small>mL (at -20°C)</small>
<b>SUM:</b>				

<b>BOTTLE TYPE:</b>	<b>BOTTLE VOLUME:</b> _____ mL
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**CALIBRATION OF THIS STANDARD:**

DATE <small>YY/MM/DD</small>	METHOD	MEASURED CONCENTRATION <small>µg PAN/ml solvent</small>	NOTES	SIGNATURE

**NOTES OF INCIDENTS THAT MAY AFFECT THE STANDARD:**

DATE <small>YY/MM/DD</small>	NOTE	SIGNATURE

**NORMAL STORAGE AND HANDLING PARAMETERS ARE LOGGED ON THE FOLLOWING PAGE.**



