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STEP PAN INTERCALIBRATION PREPARATIONS

PROJECT PLANNING PART 1

T. Krognes

NILU

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

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

PREFACE

The scientific details of the STEP PAN INTERCALIBRATION project will be reported and published shortly after execution of the intercalibration work. For the benefit of the participants and other interested parties, the admdinistrative details are reported before execution of the project.

This first part covers the development of the project plans up to and including the original STEP project proposal. All documents that are expected to have some general interest to the participants have been enclosed.

A list of the participiants with addresses, telephone and telefax numbers is included as enclosure 1.

NILU, 19 August 1990

Terje Krognes

STEP PAN CALIBRATON

By the end of July 1989 NILU started preparations for a STEP proposal concerning PAN intercalibration. The large technical difficulties of PAN calibration call for international co-operation, and the STEP program was found to be a very relevant framework. NILU originally proposed a bilateral co-operation with the JRC Ispra Establishment. After some telephone conversations, NILU sent a co-operation proposal to Ispra on 31 August 1989 (Enclosure 2).

In September 1989, T. Krognes visited Ispra in an attempt to construct a STEP proposal. It soon appeared that the plans needed to be revised, and that a larger group of participants should be included. The travel report from the visit to Ispra is included as enclosure 3.

NILU communicated by telefax and telephone with prospective participants. On 23 October 1989 a formal invitation was sent out (Enclosure 4). The response from the participants are collected in Enclosure 5.

In order to produce an acceptable project plan, NILU needed conferences with as many as possible of the participants. T. Krognes visited the CNSA in Madrid, the University of Paris XII and TNO in November 1989. The travel report is found in Enclosure 6. Based on the discussions during these visits and some more telephone conversations with the other participants, a preliminary project plan was sent to the participants in early December 1989 (Enclosure 7). Based on the preliminary plan the participants produced their STEP project proposal forms, which were forwarded to Brussels via NILU by the end of December 1989. (Some of the forms were delayed, and were for-

warded to Brussels on 8 January 1990). The complete project proposals is found in Enclosure 8.

The proposal was accepted by the Commission. Documents concerning the contract negotiation phase will be found in Part 2 of this report.

ENCLOSURES

1) Address/telephone/telefax list for the project participants.

2) Initial co-operation proposal from NILU to JRC Ispra, dated 31 August 1989. Includes short description of NILU PANalyzer.

3) Travel report, meeting at JRC Ispra 12 September to 14 September 1989.

4) Invitation to participate in STEP project proposal, dated 23 October 1989.

5) Participants' replies to project invitation.

6) Travel report, meetings at
   - CNSA, Madrid, 20-21 November 1989
   - University of Paris XII, 22 November 1989
   - TNO, Delft, 23 November 1989

7) Preliminary project description, dated 6 December 1989. Sent to participants as background material for formulation of the STEP proposal.

8) STEP project proposal "PAN INTERCALIBRATION".

ENCLOSURE 1

Address/telephone/telefax list for the project participants.

LIST OF PARTICIPANTS AND ASSOCIATED SCIENTISTS

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ENCLOSURE 2

NORSK INSTITUTT FOR LUFTFORSKNING - NORWEGIAN INSTITUTE FOR AIR RESEARCH
POSTBOKS 64 - N-2001 LILLESTRØM - NORGE

NILU

Dr. Helmut Knöppel
JRC Ispra Establishment
I-21020 Ispra,
Varese

ITALIA

Your ref.:

Our ref.:
TK/MAA/E-1000

Lillestrøm, 31 August 1989

Dear Dr. Knöppel

Thank you very much for yesterday´s telephone conversation and your quick reply by telefax this morning. I am delighted to hear that your colleagues in Brussels maintain that JRC can act as partner. The sec retary of the national Norwegian STEP coordinator has informed me that at least two EF countries need to be involved in a project. Would you please also check this out with your colleagues in Brussels?

My suggestions for a project proposal are as follows:

a. Based on experience from the construction of seven PAN instruments for a Nordic measurement programme, NILU proposes to redesign the NILU PANalyzer and construct two automated PAN instruments, one for each participant.

b. NILU proposes to construct two PAN/PPN calibrators, one for each participant.

c. NILU proposes that the JRC elucidates which other compounds of interest should be expected to be visible in the PAN chromatograms.

d. One compound known to appear after PAN in the chromatogram, is PPN (peroxypropionylnitrate). To our knowledge, little has been done to calibrate measurements of this compound in air. NILU proposes that the JRC develops methods for synthetization of a PPN standard and for calibration of this standard. The PPN standard should be usable both in hexane solution for tedlar bag dilution, and in tridecane solution for use in a calibrator instrument.

e. JRC brings PPN standards to NILU for installation in the calibrators. During a visit of approximately 1 week, the JRC receives training in the use of the NILU PANalyzer, and an intercalibration program is started.

f. NILU may help with installation of the instruments in Italy, if required by the JRC.

Enclosure: 2

g. NILU proposes a PAN/PPN intercalibration program. In addition to the first visit at NILU, the collaborating institutes should meet approximately 4 times during a year. Each of these visits may be estimated to 3-5 days duration.

h. NILU proposes that a 1 year parallell measurement program for PAN and PPN is performed in Oslo, Norway and Milano or Ispra in Italy. This should be coordinated with the intercalibration program above.

i. During the measurement program, additional peaks are expected to be found in the chromatograms. NILU proposes that laboratory experiments are included in the program to identify as many as possible of these peaks (GC-MS and/or LC-MS may be utilized).

As an appendix I include a short description of our present PANalyzer model with comments concerning the planned re-design. The calibrator is not yet outlined. The main principle is that a rather high amount of PAN (and/or PPN) is dissolved in a heavy lipid solvent such as tridecane (with a very low vapour pressure) and stored in a glass vessel at 0^{0}C. PAN will slowly vapourize from the solution and be diluted in a clean air flow. Due to thermal breakdown of PAN, the solution shall probably have to be renewed every three months or so.

I believe that the Departamento de Sanidad Ambiental in Madrid is currently operating a Carlo Erba PAN Analyzer (possibly the same prototype that was previously tested at NILU). If a third part is required in the project, this institute may possibly be interested. I have not yet contacted them. Of course, I would also welcome any suggestion from you, if you consider other collaborators. The address of the Madrid institute is:

Dr. J. de la Serna
Ministerio de Sanidad y Consumo
Instituto de Salud Carlos III
28220 Majadahonda, Madrid

Telefax 638-0613

My colleagues here at NILU confirm that the project proposal forms have not yet been distributed, but the applications must nevertheless be submitted by September 15th. For your information, I include a copy of some of the documents we have received, outlining the application format.

After attending the choir festival at Porto Torres, Sardinia, I shall arrive at Milano/Linate by Alitalia flight BM961 on Tuesday September 12th 09:55am. I hope to be able to stop over for a two day visit at the JRC (three days, if required). If any complications arise, I shall notify you as soon as possible. My passport was issued by the "Oslo Politikammer" (The Oslo Police Authority) on May 5th 1984. My passport number is E 0968766-1. I was born in Oslo on March 5th, 1957, and I am a Norwegian citizen.

Yours sincerely

Terje Krognes

Terje Krognes
Research Scientist

NILU PANALYZER

A SHORT TECHNICAL DESCRIPTION

PAN (Peroxy Acetyl Nitrate) is commonly measured by an isothermal gas chromatograph equipped with a gas sampling valve, a packed column and an ECD (Electron Capture Detector). PAN is highly reactive and thermally unstable. It must be analyzed at a temperature between 20^0C and 50^0C. This is far below the temperature range (200^0C to 300^0C) where the ECD is generally well behaved. To allow PAN measurements in background areas, the instrument sensitivity must be maximized (detection limit 30 ppt or better should be achieved). Furthermore, a maintenance free operating period of minimum 6 months should be aimed for (paper, printer cartridge may nevertheless need to be changed every third or fourth week). To achieve this, all contaminants and other interfering compounds (such as water and oxygen) must be removed from the carrier gas and/or from the sample, the analysis time and temperature must be kept low, and the instrument must be properly automated (reliable automatic re-start after power failures is essential).

In the NILU PANalyzer two valves are added to the traditional construction. One of these serves to switch out the oxygen peak (which would appear early in the chromatogram) and some contaminants that are eluted in the same time period. The other new valve will place the entire column in backflush mode before the water peak is eluted. Both water and other contaminants are thus prevented from entering the detector.

A short description of the main components included in the instrument price is given below (specifications may be changed at any time). The margin comments outline the re-design planned for 1990:

1. Incubator Termaks B4057:

A smaller unit would be preferred in new instruments

This provides a representative exterior, a sturdy frame and a temperature regulated compartment that is large enough to accomodate all temperature sensitive components of the chromatograph's flow system. A separate compartment on the left hand side accomodates power supplies and the instrument controller.

2. Pressure regulator Alfax GA-2/3:

To be omitted.

One step pressure regulator of non-lubricated metal piston type. Mounts directly onto the nitrogen bottle. Fixed outlet pressure 3 bar. The outlet fitting is Swagelok SS 316 1/8" and reducer to 1/16".

3. Pressure regulator Alfax BS-300/3:

To be replaced by absolute pressure regulator.

One step pressure regulator of non-lubricated metal bellows type. Mounted inside the temperature regulated area. Outlet pressure is adjustable up to 3 bar above the atmospheric pressure. Inlet and outlet fittings are Swagelok SS 316 1/8" with reducers to 1/16".
For airborne operation an absolute pressure regulator (referenced to vacuum) will be needed to obtain constant retention times with a variable surrounding pressure. This is not included in the present instrument.

4. Carrier gas filter:

All stainless steel construction. No O-ring seals, no teflon tape seals. Made from 20 cm of 1" SS tubing. End caps are Parker SS reducing unions 1"-1/16" with 10 µ SS frits. The cartridge is filled with activated charcoal and molecular sieve 10 Å.

5. Sample valve Valco EC6P:

Electrical valve actuators to be replaced by pneumatic.

6 port rotary valve with graphite filled PTFE rotor. 1/16" Valco fittings and standard port size 0.030". Electric actuator is included.
This valve injects the sample into the carrier gas flow.

6. Backflush valve Valco EC8P:

P-series valves to be replaced by W-series.

8 port valve as described in point 5 above. Staggered port configuration (acts as two separate 4 port valves).
This valve will connect two identical columns into the system. One will be backflushed while the other is connected between the sample valve and the detector. Due to the added flow resistance of the sample valve, the backflush flow will allways be slightly larger than the forward flow. Over time, heavy contaminants will therefore slowly migrate backwards through the columns, away from the detector.

7. Oxygen peak removal valve Valco EC4P:

4 port valve as described in point 5 above.
This valve disconnects the detector from the sample flow during the oxygen peak. The oxygen would otherwise severely overload the detector and cause chemical reactions that would leave the detector unstable for 3-5 minutes.
To be stable, the detector must be constantly fed with nitrogen carrier gas at a constant pressure, constant flow, and even a constant level of column bleeding. This is achieved by connecting the detec-

tor to the outlet of the backflush flow when it is disconnected from the sample flow. As a result of this configuration, a new sample can only be introduced when the backflush flow has become reasonably free of contaminants (total cycle time should be at least the time between sample injection and backflush multiplied by three).

8. Columns Supelco 2-1587:

Shorter column to be tested.

Two identical glass columns, 2 mm inner diameter, 1 m length, 1/4" outer diameter. Packing material is 5% Carbowax 400 on Chromosorb W-HP 80-100 mesh support. The packing material is kept in place with silanized, baked-out glass wool. Fittings are Swagelok SS-400-6-1ZV reducing unions with PTFE ferrules contacting the glass columns.

9. Detector A. I. Industrial:

Electron capture detector type number 37210. Cylindrical construction, center electrode supported by PTFE seal. Ni foil with 10 mCi ^{63}Ni. Fittings are 1/8" tube stubs extending from the SS body.

10. Mass flow controller Tylan FC-280-S:

The three continuous nitrogen flows (carrier, make-up and backflush) all enter a common cavity (constructed from 2 m of 1/4" SS tubing) and are then released to the atmosphere through a mass flow controller. This will isolate the detector chamber from fluctuations in ambient pressure.

11. Sample pump ASF:

24 VDC rubber membrane pump. This is not a clean component, but sample or carrier gas will never pass through it. It is connected to the outlet of the sample loop.

12. Sample inlet and sample loop:

Traditionally PTFE tubing has been used for these parts to avoid sample decomposition upon excessive contact with metal surfaces. To obtain a true zero level in blank samples and to minimize memory effects, these parts are now made from stainless steel. The timing of the sampling procedure is adjusted to minimize the time the sample contacts these metallic surfaces.
The sample loop is made from 56 cm SS tubing 1/8" outer diameter, 1.5 mm inner diameter. The volume is approximately 1 cm^3.

13. Tubing and fittings:

Tubing and fittings in PEEK (ketone resin) to be tested.

All internal tubing carrying sample, carrier gas, make-up gas or backflush nitrogen supply, are 1/16" SS 316 tubing with an inner diameter of 0.75 mm (regular grade, Supelco part number 2-0553).
All fittings (unions, reducing unions, tee or cross unions, reducers) are SS compression fittings (Swagelok or Valco).

14. ECD controller:

Minor redesign required.

The ECD controller is housed in a cast aluminum box 120 * 94 * 33 mm. It is mounted inside the temperature controlled area close to the ECD. All controls are operated by help of a small screw driver that is inserted through holes in the front panel. Standing current and output voltage may be read out from a digital voltmeter unit incorporated in the controller.

The controller is dedicated to a packed column chromatograph by reducing bandwidth to the minimum required. Baseline noise originating from small fluctuations in flow and pressure are reduced by a filtering time constant of 0.5 seconds.

The bias voltage (constant frequency operation) or the reference current (constant current operation) may be set manually or by an external voltage. This allows the instrument controller to automatically maintain a constant baseline level over long periods of time.

The following controls are available:

SW1: Bias voltage internal / external
Pot.1: Internal bias voltage adjustment
SW2: Input filter in CF or CC mode
Pot.2: Baseline frequency adjustment
SW3: Meter switch ref. current / output voltage
SW4: Constant current / constant frequency mode
SW5: Pulse width 3 µs / 5 µs

15. Flow controller panel:

This unit is housed in a cast aluminum box 120 * 94 * 33 mm. All controls are operated by help of a small screw driver that is inserted through holes in the front panel. The unit accepts a 15 VDC supply. 15 VDC power and 0 to 5 VDC set point control is provided to a Tylan flow controller. A digital voltmeter module may show the set point or the resulting flow, both scaled in standard ml/min.

16. Power supply 24 VDC Bentron:

To be omitted.

This is a linear power supply providing a low noise power source for the SAIA instrument controller, for the flow controller and for the ECD controller. It provides maximum 2.5 A at 24 VDC. A switched mode power supply of the same capasity would be smaller and more lightweight, but would produce more harmful high frequency noise.

17. Instrument controller SAIA PCA1.M41:

To be omitted.

A general purpose programmable logic controller with the following plug-in modules:

PCA1.R96:	Battery backed RAM module
PCA1.A21:	Relay output card
PCA1.W32:	Analog I/O card
PCA2.P05:	Handheld programming unit

This controller will retain its program even during several months of power failure. When power returns, the controller will automatically resume its operation.

The relay outputs are used to control the instrument valves and the integrator remote start function. Before each run the analog I/O module will read the baseline level and output a corrected reference voltage to provide a zero baseline level at the current frequency setting and contamination level.

The following components (or suitable substitutes) are needed to operate the instrument, but are not included in the instrument price. They should be purchased by the instrument owner in his own country:

18. Integrator HP 3396A:

To be omitted.

This new model HP integrator prints reports on 210 mm * 12" fan-fold ink-jet paper. The following cables should be ordered with the integrator:

Analog Signal Cable, General purpose spade lugs
Remote Control Cable, General purpose spade lugs

NEW COMPONENTS IN PROPOSED 1990 MODEL

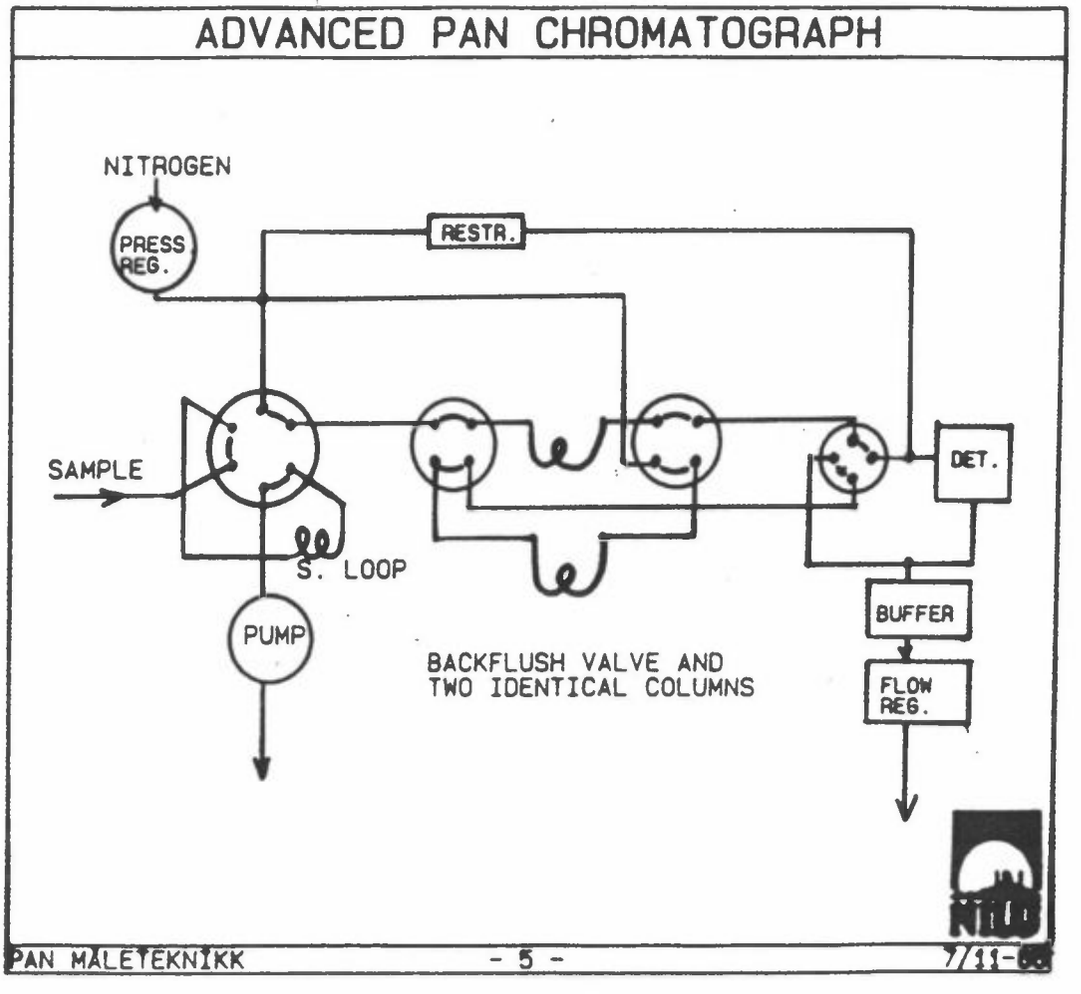
In addition to the new components commented in the margin above, some major components are likely to be changed or added. All these components will be defined as part of the instrument:

The carrier gas bottle (nitrogen 4.0) will probably be replaced by a Nitrox Ltd. nitrogen generator type ECN 400-1. This unit supplies high purity pressurized nitrogen that will be used as carrier gas and pneumatic valve actuator drive gas. We are currently discussing minor modifications with the manufacturer to ensure maximum purity.

In the list above, both the instrument controller and the signal integrator were omitted. Both these functions are now expected to be handled by an IBM-compatible PC-AT with several interface cards, MS-WINDOWS and the HP Chemstation software. Additional software routines will probably be written at NILU.

A small UPS (Un-interruptible Power Supply) unit should be included to minimize the number of power failures affecting the instrument and the computer. If available, a model with 24 VDC battery voltage will be chosen. This will enable the entire instrument to be operated directly from 28 VDC aircraft power supplies.

The weight of the complete instrument, including nitrogen generator, GC, PC and UPS should be between 90 and 100 kg. If a smaller GC oven is purchased or constructed, some 20 kg may be saved.



ENCLOSURE 3

Travel report, meeting at JRC Ispra, 12 September to 14 September 1989

TRAVEL REPORT

Visit to JRC ISPRA, Chemistry department

12-14 September 1989

Terje Krognes

NILU

INTRODUCTION

By the end of August 1989 NILU (The Norwegian Institute for Air Research) contacted the JRC Ispra (The European Communitie's Joint Research Centre at Ispra in Italy). NILU suggeste co-operation regarding a STEP (Science and Technology for Environmental Protection) project proposal concerning intercalibration for PAN (Peroxy Acetyl Nitrate) measurements.

The JRC Ispra Chemistry department headed by Dr. F. Geiss consists of 5 sectors, among these the Sector for Environmental Chemicals headed by Dr. H. Knöppel, and the Sector for Analytical Chemistry headed by Dr. G. Serrini.

After NILUs initial approach by telefax, Dr. Knöppel arranged a visit to the JRC Ispra and a meeting with Dr. Serrini. The travel expenses were covered by the NTNF (The Royal Norwegian Council for Scientific and Industrial Research).

MEETING AT JRC ISPRA 12 SEPTEMBER 1989

From JRC ISPRA: Dr. H. Knöppel
Dr. G. Serrini
Dr. Y. Libert
Dr. D. Kotzias

From NILU: T. Krognes

The STEP project proposal suggested by T. Krognes by telefax 31 August 1989 was discussed. The Sector for Analytical Chemistry (Dr. Serrini and Dr. Libert) is operating a new Carlo Erba PAN analyzer they need to establish methods for PAN calibration. The suggested project proposal however, was in some parts too ambitious. It would require too much manpower, and would require work to be done in fields with which neither JRC Ispra nor NILU are acquainted. The parties agreed that NILU should re-work the suggested project proposal and include a larger group of research institutions. Even if this results in a more ambitious project, each participating institute will have a better possibility to tailor its contribution to its specific area of experience.

TECNICAL DISCUSSIONS AT JRC ISPRA 13-14 SEPTEMBER 1989

Due to the thermal instability of PAN, a large number of technical and practical details in the working methods have a major influence on measurement and calibration results. It is therefore very important to see what other scientists do, how they do it, and with what equipement. The experience and inspiration of these two days is of great importance to my further work with PAN measurements. A few of the most important topics discussed are briefly summarized below:

- The JRC Ispra received a Carlo Erba PAN analyzer in May 1989. It is nearly identical to the Carlo Erba prototype that was tested at NILU in 1987. The column of the 1987 prototype destroyed PAN. The JRC Ispra instrument, however, has an excellent column. (Approx. 1 m x 2 mm i.Ø., 10% CW400 on Supelcoport 80/100, glass wool stoppers).

- The JRC has operated the instrument since May, but awaited fine tuning and a PAN standard from Carlo Erba. Carlo Erba on its part has awaited Dr. Ciccioli's recovery.

- Dr. Libert was concerned by observations made with synthesised PAN and during natural PAN episodes; the amount of PAN collected by bubbling the detector elute through a NaOH solution, was not proportional to the instrument PAN response. This is in accordance with NILU's assumption that PAN, due to its instability, to a large extent undergoes dissociative electron capture in the ECD. The discrepancies should be expected to be larger when analyzing for Ac than for NO_2 /NO_3 .

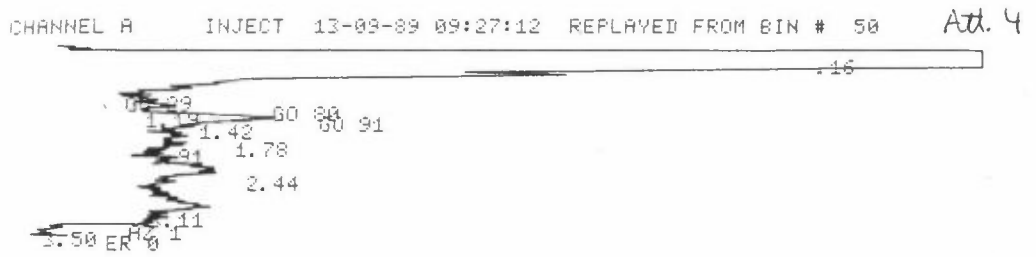
- Krognes was concerned by the apparent relationship between PAN (Peroxy Acetyl Nitrate) and PPN (Peroxy Propionyl Nitrate) in the JRC chromatograms. PPN was often at the same peak height as PAN (Figure 1). A simple experiment revealed that both peaks were probably only baseline noise. When sampling was disabled, the baseline would still have peaks twice as high as the "PAN" and "PPN" in Figure 1.

- The operating parameters were adjusted as follows:

	Before	After
Operating mode	CC	CF
Baseline frequency	-	2kHz
Reference current	1,6 nA	-
Standing current	-	0.9 nA

The signal to noise relationship was increased by a factor of approximately 40. Figure 2 shows a chromatogram that also includes the water peak. (Weather conditions were stable throughout the day, clouded with light rain and no wind. Ambient PAN concentrations should be expected to be quite stable).

- The chromatogram in Figure 2 revealed that the Spectraphysics integrator constructs a baseline from the lowest point (as indicated in Figure 2) and performs a dropline integration of later peaks. A time function was added to set the baseline at a suitable point. (the preferred function would be "Set baseline at all valley points"). Figure 3 shows an ambient air chromatogram after the adjustments.



13-09-89 09:27:12 CH= "A" P

S= 1.

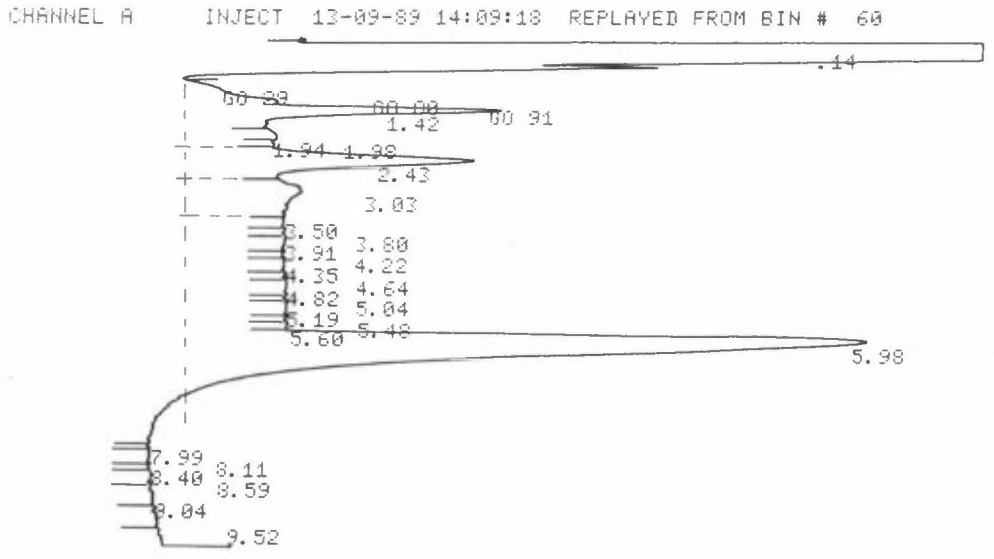
FILE 1. METHOD 5. RUN 50 INDEX 1 B

IN 50

SAMPLE 1 PANGEN BIN 50 NAME ARUN0050

NAME	PPB	RT	PK HT	BC	RF
1	0.	0.16	751479	02	
2	0.	1.19	446	02	
PANGEN	0.53	1.42	924	02	1742.004
4	0.	1.78	433	02	
5	0.	1.91	415	02	
PAN	0.119	2.44	506	02	4267.002
PPN	0.084	3.11	358	02	4266.999
8	0.	3.5	70	03	
TOTALS	0.733		754632		

Figure 1: Ambient air chromatogram from Carlo Erba PAN analyzer with initial Carlo Erba parameter sittings.



S= 1. 13-09-89 14:09:18 CH= "A" P

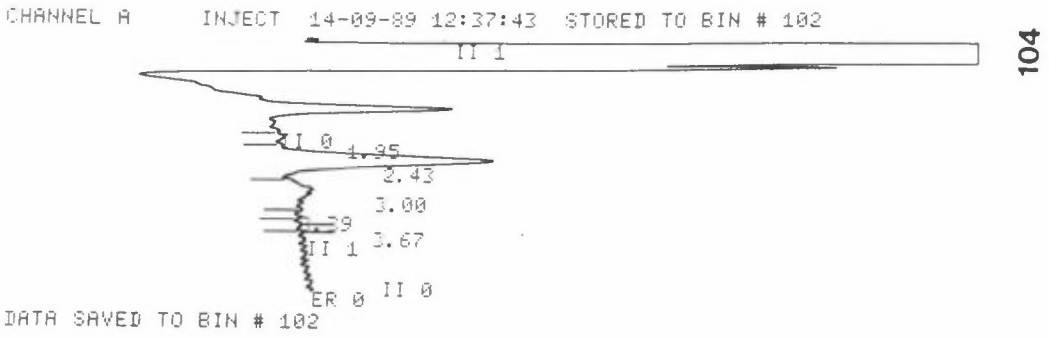
IN 60 FILE 1. METHOD 5. RUN 66 INDEX 1 B

SAMPLE 3 PPN BIN 60 NAME ARUN0060

NAME	PPB	RT	AREA BC	RF
1	0.	0.14	305374 01	
PANGEN	0.	1.42	47268 02	
3	0.	1.94	10117 02	
4	0.	1.98	6169 02	
PAN	12.776	2.43	54514 02	4267.
PPN	6.657	3.03	40869 02	6138.844
7	0.	3.5	12444 02	
8	0.	3.8	8872 02	
9	0.	3.91	16546 02	
10	0.	4.22	7514 02	
11	0.	4.35	15273 02	
12	0.	4.64	9284 02	
13	0.	4.82	17426 02	
14	0.	5.04	7187 02	
15	0.	5.19	17794 02	
16	0.	5.48	8148 02	
17	0.	5.6	8240 02	
18 WATER	0.	5.98	195878 08	
19	0.	8.11	243 06	
20	0.	8.59	346 06	
21	0.	9.04	354 07	
TOTALS	19.433		789860	

44

Figure 2: Ambient air with approximately same PAN concentration as in Figure 1. PAN analyzer now in CF with optimum settings. Integrator baseline construction is indicated.



14-09-89 12:37:43 CH= "A" PS= 1.

FILE 2. METHOD 5. RUN 82 INDEX 82 BIN 102

NAME	PPB	RT	PK HT	BC	RF
1	0.	1.95	46	02	
PAN	0.945	2.43	1127	02	1192.88
PPN	0.048	3.	130	03	2740.4
TOTALS	0.993		1303		

Figure 3: PAN chromatogram with best integrator settings.

TELEPHONE CONFERENCE WITH DR. CICCIOLI 14.SEPTEMBER 1989

Dr. Ciccioli is now recovering after his car accident, but is still not back at work. Dr. Serrini helped arrange a telephone conference with Dr. Ciccioli in his home.

During the conference Dr. Ciccioli was informed about NILU's plans for suggesting a STEP project proposal. He expressed interest for the suggestion, and asked to be included in NILUs list of potential participants.

A number of technical details were discussed. A few of these are briefly summarized below:

- Dr. Ciccioli himself prepares PAN both in gas phase and in liquid phase synthesis, and he utilizes HPLC purification. He is interested in a dynamical PAN calibration system as described by Grosjean.

- Carlo Erba has produced a limited number of PAN analyzers on a commercial basis. The instruments are based on the experience of Dr. Ciccioli. Carlo Erba still seems to depend on Dr. Ciccioli for tuning and calibration of the instruments.

- The sensitivity achieved with the Carlo Erba instruments gives a practical detection limit of approximately 50 ppt of PAN (peak height >3* baseline noise, peaks are detectable for an electronic integrator).

- The instruments are in most cases operated with the following paramters:

Detector temperature	80^0 C
Oven temperature	40^0 C
Carrier (N_2) inlet pressure	1,3 kPa
Make-up (N_2) inlet pressure	0,2 kPa
Pulse height	50 V
Pulse width	1 µs
Operation mode	CF (Constant Frequency)
Pulse frequency	2 kHZ
Back current	1-2 nA

- Dr. Ciccioli prefers not to operate the ECD at the peak sensitivity at approximately 900 Hz. He finds the detector more stable and reliable above 1000 Hz (2 kHz preferred).

- Both Dr. Ciccioli and NILU have observed that the CF (Constant Frequency) mode gives the highest sensitivity, with a negative water peak that tails severely. The CC (Constant Current) mode gives lower sensitivity, a more well behaved baseline (signal/noise ratio unaltered), and a narrow, positive water peak.

- Dr. Ciccioli operates his instruments without oxygen scrubbing or other filtering of the carrier gas. He uses ultra high purity N_2 from Matheson (<5 ppm O_2).

ENCLOSURE 4

NORSK INSTITUTT FOR LUFTFORSKNING - NORWEGIAN INSTITUTE FOR AIR RESEARCH
POSTBOKS 64 - N-2001 LILLESTRØM - NORGE
NILU

Sent to:
Dr. Penkett
Univ. of East Anglia, England
Dr. Toupence
Univ. Paris XII, France
Dr. Guicherit, c/o Dr. Hub Dideren
TNO, Delft, Holland
Dr. Juan de la Serna
Centro Nacional de Sanidad Ambiental
Majadahonda, Espana
Dr. Serrini
JRC Ispra
Dr. Rudolph
KFA Jülich
Federal Republic of Germany
Dr. Glavas
Univ. of Patras, Greece
Dr. Ciccioli
Conciglio Nacionale Ricierce
Istituto Inquinamento Atmosferico
Roma, Italy

Your ref.: Our ref.: TK/MAA/N-8728 Lillestrøm, 23 October 1989

INVITATION TO PARTICIPATE IN STEP PROJECT PROPOSAL

Enclosed please find an invitation to participate in a STEP project proposal regarding PAN (Peroxy Acetyl Nitrate) intercalibration.

We would appreciate your answer by telefax before 3 November 1989. We sincerely hope that your institute will agree to participate.

If you need further technical information, please contact our research scientist Terje Krognes.

Yours sincerely,

Harald Dovland
Director

Terje Krognes
Research Scientist

Enclosures: 1

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Office address: Elvegt. 52 LILLESTRØM
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NORWEGIAN INSTITUTE FOR AIR RESEARCH
Our ref.: TK/MAA/N-8728/20 October 1989

PROJECT PROPOSAL
INVITATION TO PARTICIPATE

A STEP TOWARDS PAN INTERCALIBRATION

PAN (Peroxy Acetyl Nitrate) is a well known component of photochemical smog and an important factor in the budget of nitrogen compounds in the atmosphere. Several groups of scientists throughout Europe now measure PAN on a regular basis, both in urban areas and in background areas. Since PAN is thermally unstable and ambient PAN concentrations are rather low (low ppb to low ppt range), both measurement and calibration is complicated. Over the years, numerous "convenient methods" for PAN calibration have been published. Our experience is that even for the most convenient methods, small experimental differences may cause large differences in results. An international intercalibration program for PAN is therefore a complicated task, and it should have been carried out already years ago to minimize systematic errors.

NILU is about to propose a PAN intercalibration project under the Commission of the European Communities STEP program. Of the 9 research areas defined within STEP, this project addresses area No. 3: "Atmospheric Processes and Air Quality". The STEP information file from the Directorate for Environment on Non-Nuclear Energies specifically lists as relevant topics: "equipment and techniques to measure trace nitrogen compounds in the troposphere" (hereunder also "intercomparison exercises"), "regional cycles of air pollutants in the Mediterranean area", and "budget of photooxidants and related species over the North Sea region".

PAN is normally measured by an on-line gas chromatographic technique using an electron capture detector. Calibration is carried out by PAN either synthesized in gas phase by UV irradiation, or in liquid phase. Gaseous PAN may be used directly, stored in gas phase, or dissolved in an organic solvent. In many cases the solution is purified by HPLC before use. The PAN yield from the synthesis and/or purification must in any case be calibrated. The PAN analyser consequently may be calibrated by the known output from a continuous or semi-continuous PAN synthesis, by

the known output from a diffusion tube containing a PAN solution, or by diluting a small amount of PAN solution in a bag of clean air.

Calibration of the PAN yield from a synthesis or PAN concentration in a solution is in most cases performed by ion chromatographic analysis of acetate or nitrite/nitrate after a hydrolysation process. At high gaseous PAN concentrations, IR-spectroscopy or a NOx-analyser may also be used.

NILU proposes to use ion chromatographic analysis of acetate after hydrolysation in a week NaOH solution as a reference for evaluation and comparison of different techniques. PAN dissolved in an organic solvent is easily hydrolysed by vigourously mixing a sample with an aqueous NaOH solution. PAN from any gaseous source may be bubbled through an NaOH solution. Thus, for all different sources of PAN, the PAN yield or PAN concentration may be measured by this single method. The ion chromatography may be performed in slightly different manners by different labs without detrimental effects to the intercomparison. The hydrolysation step requires some consideration in order to avoid uncontrolled losses of PAN. N-propylnitrate (a thermally stable internal standard) may be added to any PAN standard. It will not interfere with ion chromatographic analysis of acetate.

NILU proposes that an intercalibration program is combined with a parallel measurement program. Participants may set up a new measurement site for this purpose or make data from an existing site available to the collaborators. The intercalibration may be performed in the following manner:

1) A PAN solution is distributed to the participants at dry ice temperature. After use, the solution is returned to the co-ordinator for re-calibration.

2) The participants measure the concentration of the solution in order to compare results of the ion chromatographic analysis method.

3) The participants calibrate their own PAN source(s) with the same ion chromatographic method.

4) Each participant calibrates his PAN analyzer with PAN from at least two different types of sources, or by at least two different methods

(i.e. PAN from a liquid synthesis compared to PAN from a gaseous synthesis or one PAN solution applied through a diffusion tube compared to dilution in a bag, etc.).

NILU proposes that the project include a 6-12 month preparation period, a 12 month intercalibration and measurement period and a 12 month evaluation and reporting period. Before the proposal is forwarded to the Commision, the participiants should agree upon which elements should be included in the intercalibration program and how many times the elements should be repeated. NILU is prepared to act as project co-ordinator.

NILU is presently involved in a Nordic PAN intercalibration and measurement program. The Nordic intercalibration is focussed upon ion chromatographic calibration of a PAN standard dissolved in hexane, and GC calibration by dilution of this standard in a Tedlar bag with clean air. NILU has constructed PAN analyzers for the 5 participants (NILU included) of this program. Furthermore, NILU is operating a PAN analyzer at the Zeppelin mountain station in Ny Ålesund, Spitsbergen, and a NILU PAN analyzer will be exported to Poland in the beginning of December. Within three months NILU will start working with a temperature-stabilized diffusion tube as a continuous PAN and PPN (Peroxy Propionyl Nitrate) source.

NILU does not construct instruments for commercial purposes, but may on request provide participants with a PAN analyzer and/or a diffusion tube PAN calibrator on a net cost basis.

This invitation is forwarded to the following scientists:

Dr. Guicherit, TNO, The Netherlands
Dr. Penkett, University of East Anglia, Great Britain
Dr. Rudolph, KFA Jülich, Federal Republic of Germany
Dr. Toupence, University of Paris No. XII, France
Dr. Glavas, University of Patras, Greece
Dr. Serna, National Center of Env. Health, Madrid, Spain
Dr. Serrini, JRC, Ispra, Italy
Dr. Ciccioli, Rome, Italy

NILU respectfully asks for a reply by telefax before Friday 3 November 1989. Please include the following information:

1) A statement of intent regarding participation to work out a project proposal.

2) A short outline of the participation that may seem relevant and desirable to your institute.

3) A preliminary evaluation of the amount of work and equipment costs involved.

4) Any comments on the content of the proposed project.

5) A short description of the PAN measurement and calibration techniques currently in use by your institute.

6) A short description of the station(s) that would be used for this project, and the typical air quality of the area. Are EMEP and/or meteorological data available for this station?

Please do not hesitate to contact NILU for further information, if required. The complete project proposal must reach the commisison in Brussels before 29 December 1989. We therefore should act quickly.

ENCLOSURE 5

N-8728

TK

V

COMMISSION OF THE EUROPEAN COMMUNITIES

JOINT RESEARCH CENTRE
Ispra Establishment
I-20 Ispra (Varese) Italy

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telex 380042EUR I 324878EUR I
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TELEFAX

Sender:	Service:	Building:	telephone no.:
G. Serrini	Chemistry	29	332-789977

date: 31.10.1989	Destination: Mr. T. KROGNES Norwegian Institute for Air Research 2001 LILLESTRØM NORWAY
time:	telefax number: 0047 .6 819247
no. of pages: cover	Title of document: Participation in Step Project proposal concerning PAN intercalibration

Dear Mr. Krognes:

Concerning your kind invitation, I inform you that:

1. We intend to participate in your project proposal.
2. We are very interested to participate in a collaborative work to improve calibration of PAN analysers.
3. As you know, we have a G.C. PAN analyser (C.ERBA), I.C$_s$ (DIONEX), NO_x analysers and other analytical facilities. Belonging to EC, we don't ask money for our participation in this STEP programme.
4. A recommendation for air sampling (length and quality of tube, filter, site etc.) should be made. We are interested in your PAN calibrator.
5. Continuous measurements of PAN in air started only at the end of September of this year; till now we have no large experience in the various calibration techniques. We have tested only IC after hydrolysation of PAN.
6. Ispra can be considered as semirural region; we have an active EMEP station where atmospheric pollutants (e. g. O_3, NO, NO_2, SO_2 etc.) and meteorological parameters are continuously monitored. Other parameters could be measured, if necessary.

Best regards.

G. SERRINI Serrini

UNIVERSITY OF PATRAS

DEPARTMENT OF CHEMISTRY
SECTION OF ANALYTICAL, ENVIRONMENTAL AND APPLIED CHEMISTRY
PATRAS, GREECE

NILU
Attn: Dr. H.Dovland
and T. Krognes

2 November 1989

Your ref: TK/MAA/N-8738/30 Oct. 1989

I thank you for the invitation to participate in a proposal on PAN intercalibration and measurement.

I think it is an excellent idea and for people who have worked or are working with PAN, is almost a necessity as it will give them an evaluation of the method they use for the calibration of PAN. We therfore gladly would participate in this proposal.

Since we are currently measuring PAN in smog experiments, we do not at this time carry ambient air measurements, and we therefore calibrate our GC-ECD on a regular basis, participating in the intercalibration is almost no disturbance in our routine work. Participating however in the 12 month measurement period may be of consequence, If you insist however on the measurement period this could be performed on our campus or possibly it may be more meaningful to be carried out in Athens. These measurements would mean the operation of an additional PAN analyzer which should run completely automated. Since this instrument is not available in our institute now and further it will have to be extensively tested in our lab before it can be operated in Athens, the preparation period that you propose must be extended up to 18 months.

Summing up this paragraph I could state that in addition to intercalibration we could, if asked, do ambient air measurements in Patras, on our University campus, and possibly in Athens. Carrying out the measurements in Athens means finding a station which at this time is not available

Whereas for the intercalibration we would need only consumables, gases and chemicals of total value 3000 ECU per year, for carrying out the ambient air measurements we would need purchasing an additional GC with ECD, automated sampling valve and data logging of total value approximately 30000 ECU. The labour expenses should amount in both cases to 10000 ECU per year. Some travel expenses should also be included of the order of 2000 ECU per year. Our University requires an overhead on the total sum or above amounts of 18%.

PAN measurement: In laboratory studies we inject manually, using gas-tight syringes or injection value, varying amounts of PAN from 0.5-2 ml depending on the column we use, wide-bore HP-1 or packed. In the past however when we determined PAN in Athens be-

cause of the low sensitivity of the ECD used we had to collect in liquid N_2 larger air samples. The analysis has always been carried with GC-ECD.

The calibration of the ECD: The PAN used for this procedure is liquid PAN in tridecane, prepared according to Gaffney et al, certain volumes of this solution are injected into the smog reactor filling manifold and carried into the chamber to the desired PAN concentration. In the past we prepared PAN by photolysis of t-2-butene+NO_2+air. 2-3 ml of the gaseous PAN mixture are injected into a GC, and separated on a 4.0% QF-1+0.18 digiycerol packed calumn. The outlet of the column is connected to an NO_x chemiluminescence analyzer, home made to be operated at flow rates 30 ml/min, via a Mo-convertor heated at 325°C, for the conversion of PAN to NO. For 5 ml sample injected, this analyzer has a detection limit of 20 ppb. This detector is easily calibrated with standard NO of accurately known concentration. Therefore for our laboratory PAN samples we need no dilution of the PAN mixture. For ambient air however with typical concentrations here in Patras 0,1-0.5 ppb PAN we assume that our ECD is linear within the range 20-0.1 ppb.

Very recently an Ion Chromatograph is available in our laboratory and we plan to calibrate PAN by determining acetate and/or NO_2^- or NO_3^- anions formed in the dilute NaOH hydrolysis of PAN.

Our station in Patras would be our Chemistry Department building. From random sampling we know that the air quality reaching us depends on the wind direction, downwind or upwind from Patras, varies from 50-100 ppb ozone, 0.1-1 ppb PAN and around 30-50 ppb NO_x. Unfortunately no meteorological data are available for our site.

Please respond to our FAX number 0030-61-991996.

Sincerely yours,

S. Glavas

Sotirios Glavas

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CENTRO NACIONAL DE SANIDAD AMBIENTAL

MINISTERIO DE SANIDAD Y CONSUMO

INSTITUTO DE SALUD CARLOS III

SUBDIRECCION GENERAL DE CONTROL

Madrid, 2 de noviembre de 1989.

Dr. Harald Dovland
Director
N.I.L.U.
LILLESTROM (Noruega)

Dear Dr. Dovland:

I received your kind invitation to our National Centre to participate in a STEP project proposal, for a cooperative study and intercalibration of peroxy-Acetyl-Nitrate (PAN) among different european countries.

The "Centro Nacional de Sanidad Ambiental" has studied the plan, that agrees with one of its lines of work, and, pleased, accept your request to collaborate in it.

Nowadays we are preparing the technical information requested in your annexed paper. It will send to Dr. Krognes next monday.

Yours sincerely.

Dr. J. de la Serna.
Coordinator.
Centro Nacional de Sanidad Ambiental.

... 28220 MAJADAHONDA (Madrid) - Teléfono 638 ... - Fax 638 06 13

lpce
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To T. KROGNES, NILU, Your Ref TK/MAA/N 8728

From P. PERROS and G. TOUPANCE, LPCE

Créteil, 1989 october 31th.

PROPOSAL FOR PARTICIPATION TO THE PAN INTERCALIBRATION PROJECT.

1/ We intent to participate to a project proposal on PAN intercalibration.

2/ We use to mesure PAN on a regular basis and we are interested to test our calibration technique and analytical procedure by respect to those of other teams in Europe.

3/ Equipment 4000 ECU
Salaries 6000 ECU
Travel 5000 ECU

4/ Agreement on the general lines. We suggest a one week campaign for field intercomparison. However, difficulty of finding a laboratory in the field, large enough for 8 teams.

5/ Measurement by GC ECD on QF1/diglycerol column, direct injection of a 4ml sample, without preconcentration, limit of detectability 30 ppt, fully automated by a microcomputer. Calibration of a reference GC in the lab by IR and transportation of this GC on field in a laboratory van, under continuous operation conditions, and calibration of the field apparatus by respect to this reference GC (injection of pure gaseous PAN sample on both GC). Control calibration of the reference GC, by IR, when back in the lab.

A secondary system is also used for intermediate calibration on the field, by using preparation of PAN by UV irradiation of NO_2 + CH_3COCH_3 in controlled conditions : technique derived from MEYRAHN et al which has been tested in the lab and has been found quite convenient.

6/ We perform continuous measurements at Col du Donon (Vosges Moutains). It is a natural forested site (750 m ASL), partially influenced by the Rhein valley. Local meteorological data are available.

50

Netherlands
organization for
applied scientific
research

MT

TNO Division of Technology
for Society

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Fax. 09 47 6 819247
Mr T. Krognes
NILU
LILLESTRØM
Norway

Direct dialling
+31 15 696012

Date
November 2, 1989

Our ref.
MTD 89/2709/JCThH/cgv

Subject

Your letter

Dear Mr Krognes,

After your conversation by telephone with Mr Diederen of our institute, I have prepared the information you asked for in your telefax dated 23 October 1989. We are looking forward to meet you in Delft on the 23th of November 1989.

With kind regards,

Koos Hollander
Department of Environmental Chemistry

Enclosures
1

Annex to MTD 89/2709/JCThH/cgv

Introduction

For over a decade TNO has carried out continuous measurements of the PAN-concentrations in ambient air. The method used is the today well known on-line gas chromatografic technique with electron capture detection. The method has essentially remained unchanged since it was published (Nieboer and Van Ham, 1976).
Up to 1986 calibration of the PAN-analyzers was carried out with a high concentration, 50-300 ppm, gaseous standard after dynamic dilution down to the ppb-level at the measurement sites.
The standard was produced in our laboratory by UV-irradiation of ethylnitrate in the presence of oxygen and stored in a pressurized cylinder. The concentration of PAN was determined by gas phase infrared spectroscopy of the undiluted standard (data from Stephens, 1973). Because of the decay of the PAN-concentration in the cylinder, the IR-analyses had to be repeated before each calibration.
The facilities for producing the gaseous standard are no longer available at TNO.
From 1986 we use a diluted liquid standard of PAN in octane which is produced according the methods described by Nielsen et al. (1982) and Holdren et al. (1984). The HPLC-purification step described by Nielsen is left out of the procedure (Gaffney et al., 1984, Holdren et al., 1984). The PAN-analysers are calibrated by static dilutions made in a tedler bag with clean air, with addition of NO_2 to improve stability of PAN and with shielding from light by a dark cover.
The concentration of PAN is determined by Fourier Transform Infrared analyses of the liquid samples, based on the data of Holdren et al (1984).
FTIR was preferred over the ion chromatographic analyses of NO_3/NO_2 (Nielsen et al., 1982) because of better reproducibility.
Although the ion chromatographic determination of acetate is in principle available we have never attempted that method. It may very well be not compatible with our method of production of the liquid standard because of risidues of acetate in the octane solution which is not purified by HPLC.
Through the years we have also used permeation tubes with propylnitrate to monitor the stability of the PAN-analysers.
However, the separation of the PAN and propylnitrate peak on the gaschromatographic column used by us is insufficient to allow a proper calibration with PAN in the presence of propylnitrate.

Relevant participation

Our interest for participation results from both main elements in the project proposal: a "European" wide monitoring network for the measurement of PAN because of our current research programmes in global atmospheric chemistry and long range transboundary air pollution and the need for a well established reference method for calibration of PAN-analyzers, which is basic for the use of data from stations in different countries.

Annex to MTD 89/2709/JCThH/cgv (page 2)

As far as PAN-measurements are concerned we would like to join the programme with a new background station to be set up next year. This station, not an EMEP station of which there are only two in the Netherlands at present, will be situated in the northern part of the country. With southern winds it is downwind of major industrial areas in the Netherlands, Belgium and the Federal Republic of Germany. With northern winds on the other hand there are now upwind industrial sources.
The station is part of the National air pollution monitoring network, thus meteorological data and most probably (to be verified for security) EMEP-data will be available.
As far as calibration is concerned we are very interested in a comparision of infrared and ionchromatographic methods for primary assessment of the PAN-concentration in standards. Also the use of a diffusion tube as a continuous source of PAN is very attractive. In spite of our long experience in the dynamic volumetric generation of calibration gas mixtures with permeation and diffusion tubes as a source of the pollutant we have never thought along that line in case of PAN.

Comments on the content of the proposed project.

At this moment I do not feel the need for further comments on the measurements programme part of the proposal.
As far as calibration is concerned the main objective is the development of a reference method for calibration.
The participation should, however, not be restricted to the ion chromatographic determination of acetate alone. The incorporation of NO_3/NO_2 analysis and infrared methods *) (liquid and gas phase) could lead to one reference method and the designation of other methods to be equivalent. This would make the results benificial to most laboratories independent of available skills and analytical methods.
Such high aims, however, require a set up of the intercalibration programme from which all contributions to bias and precision from the whole calibration process can be evaluated.

With reference to the items at the bottom of page 2 of your proposal, I can imagine us to use the distributed PAN-solution and a second one prepared by ourselves:
- to calibrate the PAN-analyser;
- to measure the concentration of the solution by IC as acetate and as NO_3^-/NO_2^-;
- to measure the concentration of the solution by FTIR. One could probably oblige participants to the IC/acetate method and encourage the application of methods at present operative in the participating laboratories.

Calibration quarterly would, including a final round at the end of the one year period of cooperative measurements, result in five distributions. With a preliminary round to see if indeed everyone is ready the total would be six.
Some attention has to be given to the stability and the speed of transport of the distributed samples.

* I refer to a recent paper by Nelly Tsalkani, now at the Ministry of the Environment, Physical Planning and Public Works, Athens and Gerard Toupance on your invitation list.

Annex to MTD 89/2709/JCThH/cgv (page 3)

Preliminary estimation of costs involved.

1. Intercalibration programme	
1st year: preparation	8.000 ECU
2nd year: intercalibrations	24.000 ECU
3rd year: evaluation	8.000 ECU
3 years total	40.000 ECU
2. Measurement programma	
1st year: preparation	18.000 ECU
2nd year: measurements	24.000 ECU
3rd year: evaluation	8.000 ECU
3 years total	50.000 ECU

All costs exclusive VAT
one ECU ≈ 8 Nkr.
one ECU ≈ 2,3 Hfl.

Literature

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J. Chem. Ed., 53, pp. 351-355.

54

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Norwegian Institute for Air Research
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Name Org.

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KFA 99.18.002

Re.: PAN calibration program/STEP proposal

Dear Dr. Krognes,

Thank you for the invitation to participate in the PAN intercalibration program. I will be glad to participate since I am convinced that the main problem with reliable PAN measurements is the lack of established, reliable calibration techniques. However, we do not run a continuous PAN monitoring program at a station and concentrate on PAN measurements during campaigns in remote regions (airplane, shipborne measurement). Moreover we do not have sufficient free manpower to participate in such an extensive intercalibration program and there will be administrative problems to obtain additional manpower for the relevant period of time. For this reason I suggested to Rainer Schmidt (Meteorologie Consult GmbH, Glashütten, West Germany), who is also involved in PAN measurements in the unpolluted troposphere a joint participation in the program. I would contribute our experience and know how with PAN measurements, and our calibration and analysis systems for PAN calibration etc. Most of the manpower, the consumables, travel costs etc and costs for building a PAN chromatograph, including data processing, which have to come from the outside. R. Schmidt will sent you a short description an intended joint participation from him and our institute in the PAN calibration program. This will also include the additional costs which we will have.

Many regards,

Dr. Jochen Rudolph

meteorologieconsultgmbh
Beratungsgesellschaft
für Meteorologie
und Luftreinhaltung

Auf der Platt 47
D-6246 Glashütten 1
Telefon: (0 61 74) 6 12 40

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NORWEGIAN INSTITUTE FOR
AIR RESEARCH
Attn. Terje Krognes
P.O.Box 64

N-2001 Lillestrom

DATUM:01.11.1989
AZ :AL0111-8

Your ref. TK/MAA/N-8728

Dear Mr. Krognes,

Enclosed you will find a proposal for our participation in a STEP project regarding PAN intercalibration.

As Dr. Rudolph from KFA Juelich has informed you we offer our participation in cooperation with the Institute of Atmospheric Chemisty (Dr. Rudolph).

We would appriciate if you could send us the adequate material for preparing the final proposal.

Yours sincerely

Dr. R. Schmitt

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FAX: 06174 61436

NORWEGIAN INSTITUTE FOR
AIR RESEARCH
Attn. Terje Krognes
P.O.Box 64

N-2001 Lillestrom

DATUM:01.11.1989
AZ :AL0111-9

Dear Mr. Krognes,

we have the intention to participate in the intercalibration project for PAN.

The estimated costs for a three year period are as following:

Durable equipment:

Gaschromatograph with complete inlet system and data-recording for low temperature operation including a cryostat

DMK 100.000.--

Consumables:

Gases, chemicals, separation columns, plumbing, valves, etc.

DMK 100.000.--

Travel expenses:

DMK 55.000.--

Personal

1 qualified technician, 3 years: 3 * 10 man-months

DMK 360.000.--

Abstract of Pojekt Definition

We can offer measurements of PAN at a station near Jülich. The new instrument we plan to build as a part of this project will allow operation at other sites (e.g. Intercomparison or measurements at "Schauinsland" or at the remote Atlantic troposphere of the Canary Islands, Baseline Izania).

The possibility to include PAN-measuring techniques for airplane or shipboard operation as well as techniques with dedection limits below 5 ppt (e.g. preconcentration) should be explored. Is there a sufficient number of potential participants with relevant instrumentation?

PAN is measured by gaschromatography cobined with ECD. The gas-inlet system is automated and offers the possibility to choose between liquid calibration and a self-designed dynamic gasphase calibration (permeation device) or the calibration method developed by Warnecke and Meyrahm.

The lower detection limit is about 5 ppt (without preconcentration). The maximum time resolution is 10 minutes.

The PAN concentration (both in liquid and gas phase) is determined by hydrolysis and subsequent analysis of acetate and nitrite ions (IC and photometric methods).

Glashütten 1.11.1988

Dr. Rainer Schmitt

CENTRO NACIONAL DE SANIDAD AMBIENTAL

MINISTERIO DE SANIDAD Y CONSUMO

INSTITUTO DE SALUD CARLOS III

SUBDIRECCION GENERAL DE CONTROL

Madrid, 6 de noviembre de 1989.

Dr. Terje Krognes.
Research Scientist
N.I.L.U.
Lillestrom (Noruega)
FAX 6 - 81.92.47

Your reference. TK/MAA/N-8728

Dear Dr. Krognes:

I am sending annexed the information requested in the Fax received several days ago.

I expect you can visit us during your trip in Spain , as you announced me in your last conversation by telephone.

Yours sincerely.

Dr. J. de la Serna.
Coordinator.

Carretera de Majadahonda-Pozuelo, Km. 2 - 28220 MAJADAHONDA (Madrid) - Teléfono 6380111 - Fax 6380613

Informative note

In the year 1977, the "Centro National de Sanidad Ambiental" of the "Instituto de Salud Carlos III" was appointed as the National Reference Centre for the National Air Pollution Network in Spain, for the study of the reference and routinary analytical methodos to determine inmission values of air pollutants in the laboratories of the Spanish Network.

Since then, this Laboratory has carried out the procedings (laboratory and field studes) and their testing and standar dization for each of the principal air pollutauts.

Those analytical studies, started with SO_2 determinations (acidimetric, thorin, TCM) and particles determinations (black smoke, nephelometric, gravimetric, etc.) followed by other air pollutants, then of less importance.

At present time, the problems of air pollution varied, and oxidant compounds raised more importance in the atmosphere. Recently, the NO_2 determination is added to the Network, and, also, in some locations the survey of local and typical industrial air pollutants is increased (for exemple, fluoride).

Oxidant smog is an important air pollutant in cities in Spain, where photoxidation processes are present, as Spain is a sunny country, and the situations of oxidant smog levels have increased last years, not only in summer but along all the year.

For this reason, one of the projects of research started about two years ago in the National Centre of Environmental Health, was to prepare a study of the routinary determination of P.A.N.

Nowvadays, this project is in its first phase of study (analytical phase) and it work some rather late over the time foreseen, principally due to the removal of the Laboratory of the National Centre to the Majadahonda Area. The Laboratory has available a GC instrument (Carlo Erba) for determination of PAN. (Today it is packed for the transport to the new location in the laboratory).

The participation in the project of our institution is of the best interest in a double way : the experience on the analytical result of other participating laboratories will be profitable for our analytical tests, and, inversely, our experience and results, will be useful for the common information, getting, at end, more realistic conclussions.

In general sense, it is too early for us to comment on this project, recently considered, without a further information available for us, as the implementation of the programme is conditioned by many different elements.

For your information, our laboratory is in way of moving to a new place (Majadahonda) since a fort-night ago, and it is expected the greater part of of laboratory can work at the new location at the end of November. There, it will be situated the sampling point for PAN measurement, al-together with the other air pollutant instrumentation, in a reference station.

The new sampling site is located at Majadahonda, a town, out-skirts of Madrid (about 15 kms. far).

More over, the National Centre, carry out other research lines of work: acid rain, aerosols, V.O.C., P.A.H., transformation of nitrogen compounds, etc., some of them in conexion with PAN measurements. Also, their participation in the intercalibration exercices with other international laboratories is regular. These connections relate the international tests of each method, with those carried out in Spain by our National Centre for testing the methods of the National Network.

With reference to a preliminary evaluation of the amount of work and equipament costs involved in the project it is a short time for us to dare a sum for this question. We consider the evaluation may be divided into three periods: 1st phase for preparation; 2ndphase of measurements and 3th phase of reporting results and conclusions. It depends on the general planning of the project, and it will be very profitable an interchange of ideas.

Consiglio Nazionale delle Ricerche
AREA DELLA RICERCA DI ROMA
ISTITUTO SULL'INQUINAMENTO ATMOSFERICO

Prot. n° 602/89

AREA delle RICERCA di ROMA II 8/11/1989
Poste: Via Salaria Km. 29,300 - C.P. 10
00016 Monterotondo Stazione (Roma)
Telefono: Direzione 9005349
Segreteria 90020265
Centralino 900201

Dr. M. DOVLAND
NILU
P.O. Box 64

N 2001 LILLESTROM
(Norvegia)

Dear Dr. Dovland,

with reference to your fax TK/MAA/N-8728 to the attention of Dr. Ciccioli, I am pleased to send you some information concerning your proposal to be submitted to CEC in the framework of STEP.

Dr. Ciccioli, still on sick leave, will be pleased to share his experience with collegues in Europe. On my side, I will be pleased to assist Dr. Ciccioli and other participants if needs will arise in the future.

I keep the opportunity to send you my best regards.

Sincerely,

THE DIRECTOR
Dott. I. Allegrini

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Consiglio Nazionale delle Ricerche
AREA DELLA RICERCA DI ROMA
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PAN CALIBRATION

INFORMATION OF THE PARTICIPANT:

C.N.R. - Istituto sull'Inquinamento Atmosferico
Area della Ricerca di Roma
Via Salaria Km 29,300 - C.P. 10
00016 Monterotondo Stazione (Roma) ITALY

Project Leader: Dr. P. Ciccioli

1) STATEMENT OF INTENT

The undersigned Dr. I. Allegrini, Director of the Institute for Atmospheric Pollution of CNR, Rome, Italy, agrees on the partecipation to an European project to be developed into the Community STEP Program on calibration of PAN analyzers. The project will be managed by NILU and will include several relevant institutions in Europe with experience and skill in the said field. The undersigned agrees that NILU negotiates with the relevant bodies the technical and financial aspects of the project providing that the following terms are approved.

2) OUTLINE OF PARTICIPATION

The participation of the Institute might be foreseen in two different ways:

a) Straigh participation: The Institute will provide instruments and equipment for the measurement of PAN and will assist in the calibration by using a number of different techniques. Two different PAN analyzers will be used wich will be calibrated through several methods.

b) Intercomparison: The Institute is ready to host an intercomparison exercise where participants might meet at the Institute location to measure PAN together with a number of different atmospheric pollutants. The location is very suitable since it is downwind the city of Rome and, expecially during summer, large concentrations of PAN are expected. This would offer the opportunity to intercompare and intercalibrate analyzers and to gain experience on significant problems on the measurement since the Pilot Station of the Institute is expecially equipped for intercomparison exercises.

3) COST AND MANPOWER

Since the Institute will apply for 100% reinboursement of marginal costs, the following items should be considered in the final proposal (Costs are in KECU per three years).

Type of Cost	A (Participation)	B (Intercomparison)	A + B
Post Docs (No. 1)	60	/	= 60
Consumables	50	35	= 85
Travels	30	20	= 50
Cost of analysis	15	20	= 35
TOTAL	155	75	= 230

4) COMMENTS

The proposal is well formulated and should be considered by ECC as a priority item. Personally, I feel that it would be desirable to add the intercomparison work which has been proposed by our Institute since analyzers might work with controlled atmospheres and could give rise to serious problems in real atmospheres where interferents and potential disturbances are present.

THE DIRECTOR
Dr. I. Allegrini

ENCLOSURE 6

Travel report, meetings at:
- CNSA, Madrid, 20-21 November 1989
- University of Paris XII, 22 November 1989
- TNO, Delft, 23 November 1989

TRAVEL REPORT

Visits to
- CNSA, 20-21 November 1989 (Centro Nacional de Sanidad Ambiental, Madrid)
- University of Paris XII, 22 November 1989
- TNO, Delft, 23 November 1989

INTRODUCTION

NILU is preparing a STEP (Science and Technology for Environmental Protection) project proposal to be submitted to the Commission of the European Communities, Directorate for Environmental and Non-Nuclear Energies, by 31 December 1989. The project proposal will be titled "PAN INTERCALIBRATION" (PAN = Peroxy Acetyl Nitrate), and research groups from 7 or 8 European countries are expected to participate.

A formal invitation was forwarded to potential participants on 23 October 1989. NILU proceeded to create scetches for a practical realization of the project. NILU needed very strongly to discuss these scetches with as many participants as possible before the plans were finalized. The three institutes visited were previously not known to the project coordinator, and they could be reached within practical limits of time and cost. The following sections give brief summaries of the discussions. Also some of the technical details are included in the summaries.

MEETINGS AT CNSA, MADRID, 20-21 NOVEMBER 1989

From CNSA: Dr. Juan de la Serna
Ms. R. Fernandez Patier (Head of dep.)
Dr. T. Bomboi (PAN, GC)
Dr. J. Garcia (IC)
Mr. J. Mendez (GC)
Ms. M. Esteban (IC)

From NILU: T. Krognes

Only a few days prior to the meetings, CNSA startet transferring their activity to new premises in Majadahonda outside Madrid. Offices and laboratories were still unfinished.

CNSA received a Carlo Erba PAN analyzer in March 1989. The instrument was assembled and started in June, to see that it functioned. However, no PAN standard was available. PAN was not identified in the chromatograms. Since the lab was unfinished, the PAN instrument was in it's crate, and could not be tested during my visit. It was therefore impossible to optimize the settings for maximum sensitivity.

The CNSA expressed a firm intention to get startet with PAN measurements as soon as possible. Furthermore, the CNSA intends to partake in the intercalibration project. There was some concern that the project may require a large amount of work. From NILU's point of view it seems that most of this work would be required to gain full control over the PAN analyzer calibration, even without participation in the intercalibration.

The intercalibration project should in fact provide very valuable support to the CNSA during their work with establishing methods for PAN calibration. It was not yet decided which methods will be used by the CNSA.

The CNSA in the foreseeable future expects to have two scientists working 1/2-time with PAN measurement techniques. Two other scientists will be involved in the work on 1/4-time and 1/8-time.

Mr. T. Krognes briefly informed about NILU's activities related to PAN measurements. The main technical difficulties were described. The CNSA received a copy of NILU's overhead foils concerning ECD-theory.

A three year intercalibration project was discussed. The three main phases of preparations, intercalibration and evaluation/ reporting were outlined. The principle of terminating project phases with internal reports was discussed.

The preparation phase may be divided into three parts. These are reporting of status quo, method investigations, and a trial intercalibration. It was suggested that ambient measurement data produced by the PAN analyzes should be reported and presented as a large scale coordinated measurement program.

MEETING AT UNIVERSITY OF PARIS XII, VAL DE MARNE, 22 NOVEMBER 1989

From U.P. XII: Dr. Toupence
Dr. Perros

From NILU: Mr. T. Krognes

Dr. Toupence briefly described the PAN measurement technique used by his institute. A manual GC was constructed in 1983. In 1986 a microcomputer controlled PAN-GC was constructed. This instrument is operated in a forested area (Donon in the east of France, close to Schwarzwald) in connection with a forest decline monitoring program. The instrument is well automated, and needs attention only every second month. The separation column is packed with 0,2% diglycerol + 4,8% QF1 on Chromosorb GAW DMCS 80-100 mesh. Some problems with support inertness and/or solvent purity have been registered. Very high purity chloroform is required for coating the QF1 onto the support. The diglycerol is thereafter added dissolved in very high purity methanol. The best results were obtained with Chromosorb G support.

For calibration of the PAN analyzer, Dr. Toupence generates PAN with a known concentration in the field. Acetone and NO_2 in air is photolysed to produce PAN at a known concentration (approximately 1,6 ppm). 20-50 µl of the gas mixture is injected via a septum, producing a sample concentration of approximately 10 ppb. Adsorbtion in the intake or sample loop of the PAN analyzer will not be detected by this calibration method. The intake tube is routinely replaced twice a year. The sample pump is operated 2 minutes at 2 l/min before sample injection.

Dr. Toupence expressed strong concern about PAN loss by evaporation in the standards that are to be distributed. If a signi-

ficant portion of the PAN in a standard bottle resides in the vapour phase, it will be lost when the bottle is opened, and the standard concentration will not be reliable. Solubility of PAN in hexane, nonane and tridecane as a function of temperature is not well known.

Dr. Toupence also remarked that HPLC and/or IC is not available to all project participants. The project should not rely too heavily on methods that are too costly to acquire. For example, the Griess NO_2^- analysis method could be used in parallel with all IC calibrations, and replace IC calibration in a limited number of laboratories. According to Dr. Toupence, HPLC is only needed when the PAN standard is made from peracetic acid. Dr. Toupence prefers to calibrate a high concentration gaseous standard by IR, and to compare this to the distributed standards by GC. Krognes commented that the GC/ECD does not give a reliable comparison, as different GC's may react differently to variations in sample matrix.

It was agreed that the participants need to test the quality of all sampling and analyzing techniques involved in their PAN measurements. The overall aim of the project should be to improve the reliability of PAN calibration.

Dr. Toupence suggested and strongly recommended that a field intercomparison campaign be included in the intercalibration project. Only when the analyzers are sampling in the same ambient conditions, a true comparison of the instrument responses may be performed. A meeting in Rome was suggested. The participants should bring their instruments to Rome, install them and let them stabilize. The instruments should then be allowed to sample ambient air in parallel for at least one week. Calibration experiments should also be included. A seminar could be arranged for the participants of the field intercalibration.

A tentative list of publications to be generated by the project was discussed. Furthermore, a tentative time schedule was discussed.

MEETING AT TNO, DELFT, 23 NOVEMBER 1989

From TNO: J.C.T. Hollander
G.M. Meijer
H. Diederen (Part of the meeting)

From NILU: T. Krognes

Preliminary project plans that had been developed during the meetings with groups in Madrid and Paris, were presented and discussed. Many tehnical details of PAN measurement and calibration methods were also discussed.

TNO has performed PAN measurements for several years, mainly on a remote station in the northern part of the Netherlands, but also on a ship travelling between Europe and Latin America.

TNO works with the stationary phase QF-1 (5% QF-1 + 0,15% diglycerol) and they use carrier gas humidification by $CuSO_4$. They have sometimes a negative peak immediately after oxsygen. The negative peak sometimes disappears if the pulse width is changed. (NILU has at a later date tested a 10% QF-1 + 0,15% diglycerol column, and found that the water peak elutes immediately after oxygen. The negative peak registered at TNO is consistent with former observations at NILU that the water peak turns negative when general contamination is combined with a short pulse width).

TNO was in favour of using ion chromatography (IC) as the main method for calibration of PAN standards, but the participants should be allowed to choose between Ac^- or NO_2^-/NO_3^- analyses. The Griess method for determination of NO_2^- could be used in parallel with IC. A participant that has no access to IC methods would then not be completely shut out. It was agreed that IC/Ac^- should be strongly recommended as the reference,

and the participants should compare this to all other methods they use for PAN standard calibration.

The suggested field intercalibration project in Rome was discussed. TNO was initially opposed to this suggestion due to the costs and technical difficulties. But if the whole group of participants is in favour of the field intercalibration, also TNO will take part. As an alternative to the field intercalibration in Rome, TNO suggested that the coordinator could travel to the other participants with his PAN analyzer and perform comparative tests in each laboratory.

It was agreed that from each participant an inventory of methods to be used, is needed. Each participant should hydrolyse and calibrate his own PAN-standards and distributed standards. Each participant should also calibrate his GC with the now calibrated standards, using different application methods and standards from at least two sources.

TNO remarked that England was not included among the potential participants (Dr. Penkett later indicated that he will participate on an informal basis). TNO also remarked that 6 participants should be considered the minimum number of participants for this type of intercalibration.

ENCLOSURE 7

NORWEGIAN INSTITUTE FOR AIR RESEARCH
Our ref.: TK/MAA/N-8728/6 December 1989

1) INTRODUCTION

This document supplies information from NILU to the institutions participating in the STEP PAN intercalibration project proposal. The project outlined in this document is set up according to the participants' suggestions as they have been expressd in meetings between NILU and ISPRA, TNO Delft, Université de Paris XII and Ministerio de Sanidad y Consumo in Madrid. Furthermore, NILU has been in telephonic contact with University of Patras (Greece), CNR (Rome) and KFA (Jülich).

It is hoped that the participants with this information and with the original forms previously mailed or delivered to them, should be able to complete their parts of the STEP project proposal within 15 December, as previously discussed. Please do not hesitate to contact NILU by fax or telephone if any doubt should arise.

Dr. Penkett, University of East Anglia, Great Britain, has recently informed NILU that he will participate in the intercalibration and measurement with local funding. Since he is presently operating a Scintrex luminol NO_2/PAN analyzer, his contribution will be of great interest to the project.

2) PAN INTERCALIBRATION

A PAN intercalibration is a complicated task. As can be seen from the following sections, a wide variety of methods for standard synthesis, standard calibration and PAN GC calibration are currently in use. The instability and reactivity of PAN gives rise to numerous sources of experimental error. Furthermore, there is no established international reference standard to which a given PAN standard could be compared. A "right answer" may only be created when a significant number of participants reach comparable results and agree that all known sources of errors have been eliminated or minimized.

The proposed PAN intercalibration has 3 main phases:

Year 1: Preparation phase
Year 2: Intercalibration phase
Year 3: Evaluation/publication phase

PREPARATION PHASE

At the beginning of the project work should be focussed on the methods already established in the participating laboratories. Participants should be allowed to consolidate these methods and, if necessary, test out minor improvements. Some laboratories that have not previously performed PAN calibrations, will need to acquire some fundamental methods during this phase. The participants will prepare a report describing status quo. Each participant submits to NILU copies of the publications on which their methods are based, and detailed descriptions of the practical application of the methods, of any modifications, and of practical problems and error sources. NILU will compile this information and produce the project's internal report PREP. I.

In the second phase of preparations the participants may need to acquire or develop some additional methods in order to measure the PAN contents of their own standards and of a distributed standard by common methods. Some suggestions are given in the section INTERCOMPARISON METHODS. The participants must include in the application forms their own preferred list of methods to be utilized. The results of the second phase are reported to NILU, and NILU compiles internal report PREP. II.

The third phase of preparations is a trial distribution of PAN solution (see detailed description in INTERCOMPARISON METHODS). Only PAN in solution can be easily and safely transported. NILU proposes to distribute a PAN standard dissolved in hexane, purified by HPLC and calibrated by IC. Each participant meausure the concentration of his own standards and of the distributed standards with all methods available to the laboratory. Furthermore a PAN GC should be calibrated with the participant's own standards and with the distributed standards, utilizing all methods available to the laboratory. The results are reported by the participants and compiled by NILU to internal report PREP. III.

INTERCALIBRATION PHASE

The main element of the intercalibration phase is the PAN standard distribution with all associated standard calibrations and GC calibrations (as in the third preparation phase). The three intercalibration runs will be documented in internal reports CAL. I, CAL. II and CAL. III. Even if some participants may have periods with technical problems, it should be possible to run the project according to a pre-planned schedule. It is expected that all participants should be fully operative at least during the last two runs.

All participants will perform the GC calibration experiments on a fully automated PAN analyzer. The instruments should be running continuously during the whole intercalibration year (only with occasional stops for service or repair). During the GC calibration experiments the PAN GC should operate in its normal, automatic cycle. The calibration experiments will only occupy the PAN GC 4-8 weeks during the intercalibration year. During the remaining time the instrument will automatically produce ambient PAN measurements with exceptionally good calibration and quality control. As a result of the intercalibration these measurements will be the first set of PAN data that are usable on a European Community scale.

At the end of the intercalibration year, all participants are asked to bring their PAN analyzers and GC calibration equipment (PAN standards, syringes, tedlar bags, PAN calibrators, etc.) to a field intercalibration hosted by Dr. Alegrini in Rome. During approximately 10 days the instruments should be set up, left to stabilize for about 1 day and calibrated by the methods that have proved most successful during the previous phases. If there are unresolved discrepancies in the previous results, these should be tested again during this meeting. For approximately 5 out of the 10 days all instruments should automatically sample ambient air, connected to a common intake system. The meeting will be organized as a workshop, with common laboratory practices, presentations of results and techniques from all the participants, and technical discussions. This form of field intercalibration is technically very complicated due to the high sensitivity and (in some cases) fragility of the instruments used. But a majority of the participants maintain that such a field

intercomparison is most important to ensure validity of the intercalibration results. The participants report their individual results to NILU, and NILU compiles the internal report CAL. IV.

EVALUATION/PUBLICATION PHASE

During the third year the intercalibration results should be evaluated. If possible, standardized PAN calibration methods may be proposed as a result of the work. The following publications should be prepared:

- A comparative study of PAN calibration methods
- Field intercomparison of PAN analyzers and calibration methods

Ambient PAN data collected between intercalibration exercises should be evaluated and related to meteorological data. The following publications should be prepared:

- Regional cycles of PAN in the Mediterranean region (Patras, Ispra, Rome, Madrid)
- PAN contribution to photooxidant budget over the North Sea region (Delft, Jülich, Oslo, England)
- PAN measurements near large cities and in "background areas" in central Europe (Paris, Delft, Jülich).

To avoid errors in PAN calibration work, a large number of practical details must be considered and controlled. The inernal reports therefore must be very detailed. The publications, naturally should be in a more compact form. For each publication one of the participants should be appointed as editor.

The project phases are summed up in Table 1 below. Each phase is terminated by the distribution of an internal report.

	WEEK	PHASE	
		PREP. I	Consolidation of existing "local" methods
YEAR 1	- 6	"	Participants report to NILU
	-12	"	NILU compiles internal report
		PREP. II	Preparations of additional methods for intercomparison
	-32	"	Participants report to NILU
	-38	"	NILU compiles internal report
	40-43	PREP. III	Trial standard distribution with comparative calibrations of local and distributed standards, calibrations of GC with the same standards
	-46	"	Participants report to NILU
	-50	"	NILU compiles internal report
YEAR 2	8-11	CAL. I	First intercalibration standard distribution Standard calibrations and GC calibrations
	-14	"	Participants report to NILU
	-18	"	NILU compiles internal report
	23-26	CAL. II	Second standard distribution
	-29	"	Participiants report to NILU
	-33	"	NILU compiles internal report
	38-41	CAL. III	Third standard distribution
	-44	"	Participants report to NILU
	-48	"	NILU compiles internal report
YEAR 3	10-11	CAL. IV	Field intercalibration in Rome
	-15	"	Participants report to NILU
	-19	"	NILU compiles internal report
	-26	EV. I	Measurement data from start of year 1 until start of field intercalibration) completely calibrated, quality controlled, tabulated and distributed to participants (Internal report EV. I)
	-34	EV. II	Draft version of publications distributed from editors to participants
	-42	EV. III	Participants submit their suggestions to editors
	-50	EV. IV	Editors submit publications to appropriate journals

This schedule is preliminary. When the exact starting date is known, adjustments may be needed to ensure that the field intercalibrations in Rome is performed in a favourable season, and to make room for holidays. The participants are invited to suggest improvements to the schedule before project contracts are negotiated with the Commission.

3) PAN STANDARDS

PAN is thermally unstable and very reactive. PAN synthesis therefore generally does not yield PAN in stoechiometric relationship to the reactants, as some PAN immediately will be lost in side reactions. The resulting mixture in many cases needs purification before use.

PAN standards are for the same reason not stable over time, and it is difficult to store, handle and transport them. The PAN standard itself must be calibrated before it is used to calibrate the response of a PAN analyzer (GC). After a period of use the PAN standard must be recalibrated.

All handling of the standard (like dilution of a PAN solution into a tedlar bag for GC sampling) may cause losses of PAN due to adsorption and thermal break-down. Adsorption losses generally represent unrecoverable errors in the GC calibration.

PAN standards may have different properties due to different methods of PAN synthesis (with different impurities in the standard). Figure 1 displays different principles for PAN synthesis and PAN standard calibration. Each box may be expanded into one or several detailed method descriptions. NILU assumes that the methods currently in use by the participants are covered by the outlined paths (please inform NILU about any corrections or additions).

Due to impurities in a standard produced by a given method, one or more of the standard calibration methods may be useless for this standard. The large variety of principles involved, the large variety of detailed methods used, and the abundant possibilities of experimental errors and technical problems imply that different groups working in different countries may arrive at very different results in their PAN standard calibrations.

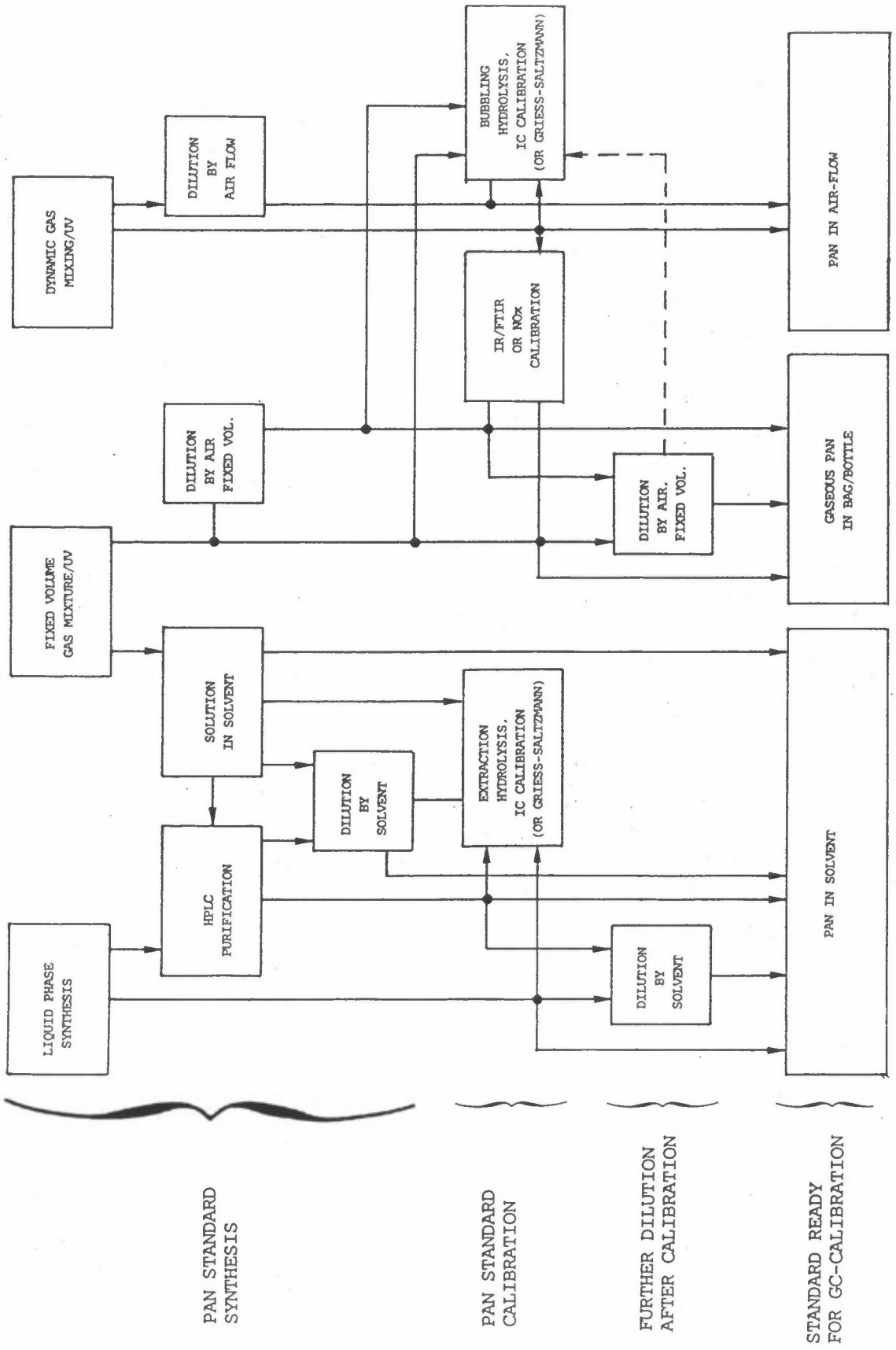

Figure 1. PAN standards may be produced and calibrated in many different ways, and may consequently have very different properties. The figure does not describe all possible combinatins, but is intended to give an overview of the most frequently used principles.

4) GC CALIBRATION

When a calibrated PAN standard is available, the PAN GC may be calibrated by several different methods (with different error sources). This again increases the possibility of differing results from different laboratories.

PAN IN AIR-FLOW

The PAN GC may sample an air-flow with a previously known PAN concentration. Thus the response of the total system (including ECD, column, valves, sample loop and sample intake) is included in the calibration factor. Due to the dynamic supply of PAN, adsorption errors in the mixing/diluting system are kept to a minimum, and the PAN output may be constant during several hours or days.

The PAN output from the mixing/diluting system may be control calibrated by bubbling hydrolysis and IC analysis. Control standard calibration by IR, FTIR or converter/NO_x-monitor methods is only possible at high PAN concentrations. Different results may be obtained with dry and moist matrix air.

GASEOUS PAN IN BAG/BOTTLE

The PAN GC may sample air with a previously known PAN concentration from a bag. Due to the static nature of the system, adsorption losses in the bag will cause unrecoverable calibration errors. The concentration will only be stable for a very limited amount of time (when stabilized by surplus NO_2) or continually decreasing. The available standard volume is limited by the bag size. Matrix air humidity may have influence on the results.

The PAN content in the bag may be control calibrated by bubbling hydrolysis and IC analysis. This may also give some information of the amount of PAN lost by adsorption in the bag.

Alternatively, an aliquote of air with known PAN concentration may be withdrawn from the bag in a syringe, and injected directly onto the PAN GC column via a septum. Adsorption losses in the syringe and in the PAN GC sample intake system will not be detected by this method.

PAN IN SOLVENT

A small amount of a very dilute PAN solution with previously known PAN concentration may be injected directly onto the PAN GC column via a septum. Alternatively, a small amount of the same solution may be injected into a tedlar bag with a previously known amount of air, thus converting it to GASEOUS PAN IN BAG (see previous section).

A more concentrated PAN solution may be converted to PAN IN AIR-FLOW in a calibrator instrument using a diffusion tube or a teflon permeation tube technique, and used as described in a previous section. Calibrators based on a solution of PAN in tridecane presently seem to be evolving into the most accurate PAN GC calibration equipment.

At any stage in the above utilization of PAN IN SOLVENT, the PAN concentration or PAN output may be control calibrated by extraction or bubbling hydrolysis and IC analysis.

ECD ANOMALIES

In the previous sections it has been stated repeatedly that knowledge of the PAN concentration is always needed prior to a GC calibration experiment. In fact, the PAN GC is not very well suited for comparison of different calibration methods. It has been stated above that matrix air humidity may strongly affect PAN adsorption and actual PAN output from a calibration device. Furthermore, PAN adsorption in the GC, and the sensitivity of the ECD itself, in some cases may vary strongly with variations in sample air humidity. This effect is known in the litterature as "the water anomaly". But the exact conditions under which

these sensitivity changes occur, are not well known. Calibration comparisons may also reveal other instrument anomalies.

5) INTERCOMPARISON METHODS

PAN STANDARD DISTRIBUTION

This is the central element of the intercalibration. It serves to establish not an absolute reference, but a reference for comparison between different laboratories.

1) Originator prepares solution of PAN in hexane
2) Originator purifies solution by HPLC
3) Originator dilutes solution and divides it into two batches
   a) 20- 30 µg PAN/ml
   b) 50-150 µg PAN/ml

   More concentrated standards may be supplied upon request
4) Originator calibrates the two batches by IC ($Ác^-$)
5) Originator dispatches samples of the two batches (~ 8 ml each, more if requested) at carbon ice temperature to the other participants by express air transport
6) Participants leave standards for acclimatisation in freezer at approximately -25°C for 24 hours
7) Participants remove three aliquotes from each batch and hydrolyse
8) Immediately after hydrolysation, the samples are analyzed for Ac^- (and, if required by the participant, also for NO_2^-/NO_3^-)
9) Approximately a week later, the participants repeat steps 7 to 8
10) The participants transfer 2 ml of each batch to new bottles (also supplied by the originator) and return these to the originator at carbon ice temperature
11) The originator recalibrates the returned sampels by IC

COMPARISON PAN IN HEXANE/PAN IN TRIDECANE

This section is included as an example of an experiment that is needed to compare two different types of PAN standards. PAN in hexane is purified by HPLC, and in many cases diluted to 100 µg PAN/cm^3 or less. This standard is best calibrated by extraction hydrolysis and IC analysis of

Ac^- or NO_2^-/NO_3^-. PAN in tridecane has not been purified by HPLC, and cannot be hydrolysed by extraction without transferring impurities from the tridecane phase. The utilization of this standard is based on evaporation of PAN from the solution.

The PAN evaporated from the tridecane may be calibrated by bubbling hydrolysis and IC analysis. To compare this with the PAN in hexane calibration, it should be demonstrated that the PAN evaporated from the tridecane may also be dissolved in hexane and then subjected to extraction hydrolysis with the same result in the subsequent IC analysis. All bubbling processes (hydrolysis or solution of PAN) should be performed with two impingers in series to demonstrate that no PAN escapes from the first impinger. Each participant should outline in his project description the experiments needed to compare his local standard and standard calibration methods to the distributed PAN in hexane standards.

6) CALCULATION OF FINANCES

Of the 8 institutions involved in the PAN intercalibraiton project proposal, ISPRA has direct community financing and cannot apply for indirect financing through STEP. Universities may calculate the marginal cost (additional cost) of the planned project activity and apply for 100% reimbursement of this sum. Other research institutions and commercial companies may apply for reimbursement of up to 50% of their calculated expenses.

Each participant should apply for reimbursement of not more than ECU 100 000,- (labour, durable equipment and consumables includes) for the total project period of 3 years. As project co-ordinator NILU will have a considerable amount of extra work (both experimental and paper work), and will apply for reimbursement of ECU 150 000.-. Since three of the participants are universities, the total calculated cost of the project is approximately ECU 1 300 000.-, of which we will apply for reimbursement of ECU 750 000.-. Given the technical difficulties of the project, the equipment needed and the amount of work involved, this is not a large sum. But we must consider ECU 750 000.- a realistic limit for the project size.

Each participant should include in his calculations ECU 2 000.- for the transport of PAN standards. Furthermore, each participant should be prepared to spend approximately ECU 5 000.- on a cooling circulation bath, a flow controller and some glass equipment for a PAN calibrator to be used with PAN in tridecane. This will probably be the best alternative if the planned PAN in hexane distribution should prove unreliable.

ENCLOSURE 8

NORSK INSTITUTT FOR LUFTFORSKNING - NORWEGIAN INSTITUTE FOR AIR RESEARCH
POSTBOKS 64 - N-2001 LILLESTRØM - NORGE

Commission of the European Communities
Att.: Dr. Angeletti
Directorate General for Science,
Research and Development
Directorate XII-B-3
Rue Montoyer 75

B-1040 BRUSSELS
BELGIUM

Your ref.: | Our ref.: TK/MAA/E-1000 | Lillestrøm, 28 December 1989

Dear Dr. Angeletti

RE.: STEP PROJECT PROPOSAL

Please find enclosed a STEP project proposal titled PAN INTERCALIBRATION. We regret that some participant forms have been delayed in the post due to the Christmas rush. The following forms will be forwarded to the commission as soon as possible:

- Participant 06, pages 8-12
  ARD = Atmospheric Research Division
  Swedish Environmental Protection Agency
  Dr. Pedro Oyola

- Participant 08, pages 8-12
  CNSA = Centro Nacional de Sanidad Ambiental
  Instituto de Salud Carlos III
  Madrid
  Dr. Rosalia Fernandez Patier

Yours sincerely

Harald Dovland
Director

Terje Krognes
Scientist

Enclosures: 1

NORSK INSTITUTT FOR LUFTFORSKNING - NORWEGIAN INSTITUTE FOR AIR RESEARCH
POSTBOKS 64 - N-2001 LILLESTRØM - NORGE

Commission of the European Communities
Att.: Dr. Angeletti
Directorate General for Science,
Research and Development
Directorate XII-B-3
Rue Montoyer 75

B-1040 BRUSSELS
BELGIUM

Your ref.: | Our ref.: TK/MAA/E-1000 | Lillestrøm, 8 January 1990

Dear Dr. Angeletti

RE.: STEP PROJECT PROPOSAL, DELAYED PAGES

Please find enclosed the pages listed below and insert them in our STEP proposal titled PAN INTERCALIBRATION. We apologize for the delay.

- Participant 06,pages 8-12
  ARD = Atmospheric Research Division
  Swedish Environmental Protection Agency
  Dr. Pedro Oyola

- Participant 08, pages 8-12
  CNSA = Centro Nacional de Sanidad Ambiental
  Instituto de Salud Carlos III
  Madrid
  Dr. Rosalia Fernandez Patier

Yours sincerely

Harald Dovland
Director

Terje Krognes
Scientist

Enclosures: 1

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: 3 30 83 27

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COMMISSION OF THE EUROPEAN COMMUNITIES

Directorate General XII
Science, Research and Development

Project proposal for financial support
from the EC in respect of Community Activities
in the Field of Research and Technological Development

STEP

Science and **T**echnology
for
Environmental **P**rotection

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TITLE OF THE PROPOSAL

For technical information contact Directorate XII-E-1

PAN INTERCALIBRATION

Project proposal relates to: (see information package)

AREAS: 1. [ ] 2. [ ] 3. [X] 4. [ ] 5. [ ] 6. [ ] 7. [ ] 8. [ ] 9. [ ]

COMMENTS: PAN = PEROXY ACETYL NITRATE (A PHOTOOXYDANT AND A TRACE NITROGEN COMPOUND)

Please complete this form
accurately
using a typewriter (10 characters/inch)

To be returned to:

Commission of the European Communities
Directorate General for Science,
Research and Development
Directorate XII-B-3
Rue Montoyer 75
B-1040 Brussels

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Proposal number PL [ ]

Postmark [ ]

Acknowledgement sent on: [ ]

P.A. [ ] [ ] [ ] [ ]

[ ]

[ ]

PART 1 - PROPOSAL SYNOPSIS

94

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PARTICIPANT NUMBER

ABBREVIATED NAME (e.g. Acronym) OF ORGANISATION ACTING AS COORDINATOR

01 NILU [C]

COUNTRY: NORWAY CODE NO [ ]

ABBREVIATED NAMES (e.g. Acronym) of other INTENDED CONTRACTORS (PARTNERS) **(CR)**, ASSOCIATED CONTRACTORS **(AC)** AND MAJOR SUBCONTRACTORS **(SC)**

		CR	AC	SC
02	UNIVERSITY PARIS XII	X		
	COUNTRY: FRANCE CODE FR	LINKED TO PARTICIPANT (number e.g. 01):		
03	UNIVERSITY OF PATRAS	X		
	COUNTRY: GREECE CODE GR	LINKED TO PARTICIPANT:		
04	TNO	X		
	COUNTRY: THE NETHERLANDS CODE NL	LINKED TO PARTICIPANT:		
05	METEOROLOGIECONSULT	X		
	COUNTRY: FED. REP. OF GERMANY CODE DE	LINKED TO PARTICIPANT:		
06	ARD	X		
	COUNTRY: SWEDEN CODE SE	LINKED TO PARTICIPANT:		
07	CNR	X		
	COUNTRY: ITALY CODE IT	LINKED TO PARTICIPANT:		
08	CNSA	X		
	COUNTRY: SPAIN CODE ES	LINKED TO PARTICIPANT:		
09				
	COUNTRY: CODE	LINKED TO PARTICIPANT:		

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PART 1 (continuation)

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RESOURCES NECESSARY TO CARRY OUT THE PROPOSED PROJECT

START DATE 01-05-89 DURATION (months) 36 **MAXIMUM** 36 months

Breakdown of estimated total cost by participant specified on the corresponding page 2

PARTICIPANT NUMBER		NATIONAL CURRENCY TOTAL	CURRENCY CODE	ECU TOTAL	EC CONTRIBUTION
01	COORDINATOR:	2572000	NKR	343000	170000
02		800000	FRF	100000	100000
03		22612000	GRD	125622	125622
04		483000	NLG	210000	105000
05		942430	DEM	464251	232000
06		1150000	SEK	153000	76500
07		151500000	ITL	101000	101000
08		28000000	ESP	214385	107692
09					
	TOTAL COST (ECU)			1712258	
	FINANCIAL CONTRIBUTION REQUESTED FROM EC (ECU)				1017814

EXPECTED FINANCIAL SOURCES FOR COSTS NOT SOUGHT FROM EC:

Participants: [X]

Third Parties: State Public: [X] Private: [ ] Mixture: [ ]

Has the proposal or a similar project previously been submitted to the EC for financial support?

NO: [X] YES: [ ]

If YES, specify details of the date, Directorate General, support mechanism and outcome

[ ][ ][ ][ ][ ][ ][ ][ ][ ]

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96 PART 1 (continuation)

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SHORT DESCRIPTION OF THE PROPOSAL (ABSTRACT)

PAN is a higly reactive and thermally unstable photooxydant (Peroxy Acetyl Nitrate). It is important as a reservoir for nitrogen oxides in the atmosphere and as an interference in NOx-measurements. PAN measurement and calibration of PAN analyzers is difficult. No reference standard exists, as PAN standards are unstable. The present intercalibration proposal involves an intercomparison of the wide variety of calibration methods presently in use. The participants will calibrate PAN standards and then use the standards for calibration of PAN analyzers. The experiments will be performed with local PAN standards and with standards distributed from the co-ordinator (at carbon ice temperature). Automatic PAN analyzers are part of the intercalibration equipment. Between intercalibration experiments these instruments will produce ambient PAN measurements. Results of the intercalibration and the measurements will be published in reviewed journals.

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PART 1 (Continuation)

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ALLOCATION OF TASKS BETWEEN PARTICIPANTS

Intercalibration experiments will take place in the local laboratories of each participant. Each participant will perform PAN standard calibrations and PAN analyzer calibrations with his own methods and with additional methods for intercomparison. Each participant will report his results to the co-ordinator. Most participants will act as editor for one of the resulting publications. The co-ordinator will also act as editor for the internal reports, and will calibrate and distribute control standards to the participants. A 10 day field intercalibration campaign will be hosted by the CNR in Rome.

KEYWORDS (please use SPINES thesaurus)

INTERCALIBRATION

PHOTOOXIDANTS, PEROXYACETYLNITRATE

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We certify that the proposal details set out in Parts 1 and 2 are correct, that we will act as the coordinator in the proposed project, and that we are authorised to act as the coordinator.

	(authorised Scientific Official)	(authorised Administrative Official)
Name:	T. . KROGNES	H. . ODVLAND
Status:	SCIENTIST	DIRECTOR
Date:	28-12-1989	28-12-1989
Signature:	Terje Krognes	H Odvland

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PART 2 - DETAILED DESCRIPTION OF THE PROPOSED PROJECT:

TO INCLUDE

1 — the work to be carried out,
2 — the work programme including the methodology and manpower resources for each task, the duration, target and review dates, milestones, bar charts and evaluation criteria for monitoring the progress of the research,
3 — the state of the art,
4 — the objectives of the proposed project,
5 — the economic, social or technical benefits to the EC and relevance to EC policies
6 — the justification for requiring financial support for the proposed project **at Community level,**
7 — the relation to other EC RTD programmes or known RTD projects,
8 — the detailed distribution of tasks amongst participating organisations and the nature of the collaborative links,
9 — the complementarity between the participating organisations, the expertise to be contributed, and the benefits to be gained from the collaboration,
10 — the degree of innovation and expected achievements of the proposed project,
11 — recent publications by the proposers relevant to the proposed project.

IMPORTANT

For optical reading and evaluation the information provided must be referenced by the numbers specified above.

1 WORK TO BE CARRIED OUT

A PAN intercalibration on a European Community scale is the dominating part of the proposed project. In addition the project will yield well calibrated PAN data that are suitable for evaluation of PAN concentrations in ambient air on a European Community scale. The following work is planned:

- Detailed reporting among participant of status quo

- Preparation of methods already established in the participating laboratories

- Laboratories acquire additional methods for intercomparison purposes

- PAN standards are calibrated by the co-ordinator, distributed to the participants, calibrated by the participants, used for PAN GC calibration by the participants, and returned to the co-ordinator for re-calibration. This procedure is performed four times over a period of a year; one trial run and three intercalibration runs.

- The participants will bring their PAN analyzers and field calibration equipment to Rome for a 10 day field intercalibration campaign and comparative measurement session organized as a workshop.

- All results will be published in reviewed journals.

DETAILED DESCRIPTION OF THE PROPOSED PROJECT
(continuation)

Page 1 of 14

- During the year of intercalibrations the instruments will also produce well calibrated ambient PAN data. These data will be evaluated and published in reviewed journals.

- Throughout the project, internal reporting of well defined project phases will be used as milestones.

2 WORK PROGRAMME

The proposed PAN intercalibration has 3 main phases:

Year 1: Preparation phase
Year 2: Intercalibration phase
Year 3: Evaluation/publication phase

PREPARATION PHASE

At the beginning of the project work should be focussed on the methods already established in the participating laboratories. Participants should be allowed to consolidate these methods and, if necessary, test out minor improvements. Some laboratories that have not previously performed PAN calibrations, will need to acquire some fundamental methods during this phase. The participants will prepare a report describing status quo. Each participant submits to NILU copies of the publications on which their methods are based, and detailed descriptions of the practical application of the methods, of any modifications, and of practical problems and error sources. NILU will compile this information and produce the project's internal report PREP. I.

In the second phase of preparations the participants may need to acquire or develop some additional methods in order to measure the PAN contents of their own standards and of a distributed standard by common methods. The results of the second phase are reported to NILU, and NILU compiles internal report PREP. II.

The third phase of preparations is a trial distribution of PAN solution (see detailed description in PAN STANDARD DISTRIBUTION below). Only PAN in solution can be easily and safely transported. NILU proposes to distribute a PAN standard dissolved in hexane, purified by HPLC and calibrated by IC. Each participant meausure the concentration of his own standards and of the distributed standards with all methods

100 PART 2 (continuation)

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DETAILED DESCRIPTION OF THE PROPOSED PROJECT
(continuation)

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available to the laboratory. Furthermore a PAN GC should be calibrated with the participant's own standards and with the distributed standards, utilizing all methods available to the laboratory. The results are reported by the participants and compiled by NILU to internal report PREP. III.

INTERCALIBRATION PHASE

The main element of the intercalibration phase is the PAN standard distribution with all associated standard calibrations and GC calibrations (as in the third preparation phase). The three intercalibration runs will be documented in internal reports CAL. I, CAL. II and CAL. III. Even if some participants may have periods with technical problems, it should be possible to run the project according to a preplanned schedule. It is expected that all participants should be fully operative at least during the last two runs.

All participants will perform the GC calibration experiments on a fully automated PAN analyzer. The instruments should be running continuously during the whole intercalibration year (only with occasional stops for service or repair). During the GC calibration experiments the PAN GC should operate in its normal, automatic cycle. The calibration experiments will only occupy the PAN GC 4-8 weeks during the intercalibration year. During the remaining time the instrument will automatically produce ambient PAN measurements with exceptionally good calibration and quality control. As a result of the intercalibration these measurements will be the first set of PAN data that are usable on a European Community scale.

At the end of the intercalibration year, all participants are asked to bring their PAN analyzers and GC calibration equipment (PAN standards, syringes, tedlar bags, PAN calibrators, etc.) to a field intercalibration hosted by Dr. Alegrini in Rome. During approximately 10 days the instruments should be set up, left to stabilize for about 1 day and calibrated by the methods that have proved most successful during the previous phases. If there are unresolved discrepancies in the previous results, these should be tested again during this meeting. For approximately 5 out of the 10 days all instruments should automatically sample ambient air, connected to a common intake system. The meeting will be organized as a workshop, with common laboratory prac-

PART 2 (continuation)

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DETAILED DESCRIPTION OF THE PROPOSED PROJECT
(continuation)

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~~tices,~~ presentations of results and techniques from all the participants, and technical discussions. This form of field intercalibration is technically very complicated due to the high sensitivity and (in some cases) fragility of the instruments used. But a majority of the participants maintain that such a field intercomparison is most important to ensure validity of the intercalibration results. The participants report their individual results to NILU, and NILU compiles the internal report CAL. IV.

EVALUATION/PUBLICATION PHASE

During the third year the intercalibration results should be evaluated. If possible, standardized PAN calibration methods may be proposed as a result of the work. The following publications should be prepared:

- A comparative study of PAN calibration methods.
- Field intercomparison of PAN analyzers and calibration methods

Ambient PAN data collected between intercalibration exercises should be evaluated and related to meteorological data. The following publications should be prepared:

- Regional cycles of PAN in the Mediterranean region (Patras, Ispra, Rome, Madrid)
- PAN contribution to photooxidant budget over the North Sea region (Delft, Jülich, Oslo, England)
- PAN measurements near large cities and in "background areas" in central Europe (Paris, Delft, Jülich).

To avoid erros in PAN calibration work, a large number of practical details must be considered and controlled. The internal reports therefore must be very detailed. The publications, naturally should be in a more compact form. For each publication one of the participants should be appointed as editor.

The project phases are summed up in Table 1 below. Each phase is terminated by the distribution of an internal report.

This schedule is preliminary. When the exact starting date is known, adjustments may be needed to ensure that the field

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DETAILED DESCRIPTION OF THE PROPOSED PROJECT
(continuation)

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intercalibration in Rome is performed in a favourable season, and to make room for holidays.

Table 1: Summary of project phases

	WEEK	PHASE	
		PREP. I	Consolidation of existing "local" methods.
YEAR 1	- 6	"	Participants report to NILU.
	-12	"	NILU compiles internal report.
		PREP. II	Preparations of additional methods for intercomparison purposes.
	-32	"	Participants report to NILU.
	-38	"	NILU compiles internal report.
	40-43	PREP. III	Trial standard distribution with comparative calibrations of local an distributed standards, calibrations of GC with the same standards.
	-46	"	Participants report to NILU.
	-50	"	NILU compiles internal report.
YEAR 2	8-11	CAL. I	First intercalibration standard distribution. Standard calibrations and GC calibrations.
	-14	"	Participants report to NILU.
	-18	"	NILU compiles internal report.
	23-26	CAL. II	Second standard distribution.
	-29	"	Participants report to NILU.
	-33	"	NILU compiles internal report.
	38-41	CAL. III	Third standard distribution.
	-44		Participants report to NILU.
	-48		NILU compiles internal report.
YEAR 3	10-11	CAL. IV	Field intercalibration in Rome.
	-15		Participants report to NILU.
	-19		NILU compiles internal report.

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DETAILED DESCRIPTION OF THE PROPOSED PROJECT
(continuation)

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-26	EV. I	Measurement data from start of year 1 until start of field intercalibration) completely calibrated, quality controlled, tabulated and distributed to participants (Internal report EV. I).
-34	EV. II	Draft version of publications distributed from editors to participants.
-42	EV. III	Participants submit their suggestions to editors.
-50	EV. IV	Editors submit publications to appropriate journals.

PAN STANDARD DISTRIBUTION

This is the central element of the intercalibration. It serves to establish not an absolute reference, but a reference for comparison between different laboratories.

1) Originator prepares solution of PAN in hexane
2) Originator purifies solution by HPLC
3) Originator dilutes solution and divides it into two batches
   a) 20- 30 µg PAN/ml
   b) 50-150 µg PAN/ml
   More concentrated standards may be supplied upon request
4) Originator calibrates the two batches by IC (Ac^-)
5) Originator dispatches samples of the two batches (~ 8 ml each, more if requested) at carbon ice temperature to the other participants by express air transport
6) Participants leave standards for acclimatisation in freezer at approximately -25°C for 24 hours
7) Participants remove three aliquotes from each batch and hydrolyse
8) Immediately after hydrolysation, the samples are analyzed for Ac^- (and, if required by the participant, also for NO_2^- / NO_3^-)
9) Approximately a week later, the participants repeat steps 7 to 8

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DETAILED DESCRIPTION OF THE PROPOSED PROJECT
(continuation)

10) The participants transfer 2 ml of each batch to new bottles (also supplied by the originator) and return these to the originator at carbon ice temperature
11) The originator recalibrates the returned samples by IC

Even at the low temperatures involved, evaporation of PAN and/or hexane from the standards may cause significant concentration errors. Such problems may be solved by shipping larger amounts of standards in bottles that are always filled to the top, or by increasing concentrations, or by shipping tridecane solutions that are frozen solid. These details will be worked out during the preparation phase.

3-THE STATE OF THE ART

PAN INTERCALIBRATION

A PAN intercalibration is a complicated task. As can be seen from the following sections, a wide variety of methods for standard synthesis, standard calibration and PAN GC calibration are currently in use. The instability and reactivity of PAN gives rise to numerous sources of experimental error. Furthermore, there is no established international reference standard to which a given PAN standard could be compared. A "right answer" may only be created when a significant number of participants reach comparable results and agree that all known sources of errors have been eliminated or minimized.

PAN STANDARDS

PAN is thermally unstable and very reactive. PAN synthesis therefore generally does not yield PAN in stoechiometric relationship to the reactants, as some PAN immediately will be lost in side reactions. The resulting mixture in many cases needs purification before use.

PAN standards are for the same reason not stable over time, and it is difficult to store, handle and transport them. The PAN standard itself must be calibrated before it is used to calibrate the response of a PAN analyzer (GC). After a period of use the PAN standard must be recalibrated.

All handling of the standard (like dilution of a PAN solution into a tedlar bag for GC sampling) may cause losses of

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DETAILED DESCRIPTION OF THE PROPOSED PROJECT
(continuation)

Page 7 of 14

PAN due to adsorption and thermal break-down. Adsorption losses generally represent unrecoverable errors in the GC calibration. All dilution of PAN standards must be performed with all liquids at -25°C. At this temperature the volumetric calibration of glassware is not valid. Polypropylene pipette tips should be used to minimize heat transfer.

PAN standards may have different properties due to different methods of PAN synthesis (with different impurities in the standard). Figure 1 displays different principles for PAN synthesis and PAN standard calibration. Each box may be expanded into one or several detailed method descriptions.

Due to impurities in a standard produced by a given method, one or more of the standard calibration methods may be useless for this standard. The large variety of principles involved, the large variety of detailed methods used, and the abundant possibilities of experimental errors and technical problems imply that different groups working in different countries may arrive at very different results in their PAN standard calibrations.

GC CALIBRATION

When a calibrated PAN standard is available, the PAN GC may be calibrated by several different methods (with different error sources). This again increases the possibility of differing results from different laboratories. The following sections describe GC calibration with different types of PAN standards.

PAN IN AIR-FLOW

The PAN GC may sample an air-flow with a previously known PAN concentration. Thus the response of the total system (including ECD, column, valves, sample loop and sample intake) is included in the calibration factor. Due to the dynamic supply of PAN, adsorption errors in the mixing/diluting system are kept to a minimum, and the PAN output may be constant during several hours or days.

The PAN output from the mixing/diluting system may be control calibrated by bubbling hydrolysis and IC analysis. Control standard calibration by IR, FTIR or converter/NOx-

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106 PART 2 (continuation)

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DETAILED DESCRIPTION OF THE PROPOSED PROJECT
(continuation)

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monitor methods is only possible at high PAN concentrations. Different results may be obtained with dry and moist matrix air.

GASEOUS PAN IN BAG/BOTTLE

The PAN GC may sample air with a previously known PAN concentration from a bag. Due to the static nature of the system, adsorption losses in the bag will cause unrecoverable calibration errors. The concentration will only be stable for a very limited amount of time (when stabilized by surplus NO_2) or continually decreasing. The available standard volume is limited by the bag size. Matrix air humidity may have influence on the results.

The PAN content in the bag may be control calibrated by bubbling hydrolysis and IC analysis. This may also give some information of the amount of PAN lost by adsorption in the bag.

Alternatively, an aliquote of air with known PAN concentration may be withdrawn from the bag in a syringe, and injected directly onto the PAN GC column via a septum. Adsorption losses in the syringe and in the PAN GC sample intake system will not be detected by this method.

PAN IN SOLVENT

A small amount of a very dilute PAN solution with previously known PAN concentration may be injected directly onto the PAN GC column via a septum. Alternatively, a small amount of the same solution may be injected into a tedlar bag with a previously known amount of air, thus converting it to GASEOUS PAN IN BAG (see previous section).

A more concentrated PAN solution may be converted to PAN IN AIR-FLOW in a calibrator instrument using a diffusion tube or a teflon permeation tube technique, and used as described in a previous section. Calibrators based on a solution of PAN in tridecane presently seem to be evolving into the most accurate PAN GC calibration equipment.

DETAILED DESCRIPTION OF THE PROPOSED PROJECT
(continuation)

At any stage in the above utilization of PAN IN SOLVENT, the PAN concentration or PAN output may be control calibrated by extraction or bubbling hydrolysis and IC analysis.

ECD ANOMALIES

In the previous sections it has been stated repeatedly that knowledge of the PAN concentration is always needed prior to a GC calibration experiment. In fact, the PAN GC is not very well suited for comparison of different calibration methods. It has been stated above that matrix air humidity may strongly affect PAN adsorption and actual PAN output from a calibration device. Furthermore, PAN adsorption in the GC, and the sensitivity of the ECD itself, in some cases may vary strongly with variations in sample air humidity. This effect is known in the litterature as "the water anomaly". But the exact conditions under which these sensitivity changes occur, are not well known. Calibration comparisons may also reveal other instrument anomalies.

4-THE OBJECTIVES OF THE PROPOSED PROJECT

In the previous section (the state of the art) an overview was given of the different principles commonly used. During the first project phase the participants will report the detailed pratical methods they use. Through a number of intercalibration and intercomparison experiments the participants should be able to reach an agreement as to the accuracy and suitability of the various methods. If the experiments clearly indicate that some methods are sufficiently reliable, the participants may agree to suggest a set of standardised methods for PAN calibration.

An absolute PAN reference does not exist, and will not be constructed within this project. The aim of the project is to enable all the participants to calibrate a PAN standard and a PAN analyzer with errors not larger than $\pm$10% of the true value. Given the complexity of the task and the technical difficulties involved in handling PAN standards, the actual percent value of error limits obtained is not essential. The most important point is the ability to state that all significant error sources have been identified and controlled.

108 PART 2 (continuation)

FOR COMMISSION USE

EN G1 105159 [ ] [G] [ ]

DETAILED DESCRIPTION OF THE PROPOSED PROJECT
(continuation)

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The project will for the first time create a European platform for comparison of PAN data. The project will also yield a 1 year set of ambient PAN data from a European network of measurement stations.

5-THE ECONOMIC, SOCIAL OR TECHNICAL BENEFITS TO THE EC

PAN is a nitrogen oxide, and is an important reservoir for nitrogen oxides in the atmosphere. It is suspected to be a significant interference in most normal NOx-measurements. PAN is therefore one of the most important trace nitrogen compounds in the troposphere. Increased knowledge of PAN is essential to both measurement and modelling of NOx and NOy behaviour.

PAN is furthermore a significant component in "regional cycles of air pollutants in the Mediterranean area" and in the "budget of photooxidants and related species over the North Sea region". The projects will yield one year of measurement data for these two areas mentioned under the STEP research are 3A, Tropospheric Chemistry.

6-JUSTIFICATION FOR SUPPORT AT COMMUNITY LEVEL

Accurate calibration of PAN measurements is relevant to the assessment of NOx and oxidant budgets on a Community level. Even if much knowledge of PAN calibration is available in individual research groups, results may differ widely due to the large technical and practical problems involved. The lack of an international PAN reference make it impossible to detect such discrepancies. A Community level effort is required to reveal discrepancies, to surmount technical difficulties, and to create an international platform of reference for PAN calibrations.

7-RELATION TO OTHER KNOWN RTD PROJECTS

PAN is a second priority parameter in the TOR (Troposheric Ozone Research) programme. (Several participants in TOR now maintain that PAN should be given first priority.) Only a limited number of TOR participants presently measure PAN. The proposed STEP project will be of great benefit to future PAN measurements within the TOR programme.

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PART 2 (continuation)

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DETAILED DESCRIPTION OF THE PROPOSED PROJECT
(continuation)

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During 1989 a Nordic PAN intercalibration has been performed with 5 participants. The amount of experimental work performed was on a much smaller scale than the proposed STEP project. The Nordic intercalibration may be viewed as a natural preparation to a larger scale European intercalibration project.

8-DETAILED DISTRIBUTION OF TASKS

The co-ordinator will act as editor for the internal reports, and as welll write his own contributions to the same reports. The participants will all describe in detail their own work for the internal work. The editor function for the publications will be distributed between the participants at a later date.

Also the experimental work will be well distributed between participants, as each participant will perform calibration experiments and control experiments to his own capacity with the distributed PAN standards. Earch participant will use his own established methods plus additional methods for intercomparison purposes. The co-ordinator will have an extra load of experimental work with preparing, calibrating, distributing and re-calibrating the standards.

Dr. Alegrini in Rome will have some extra work with hosting the 10 day field intercalibration campaign. The co-ordinator will host a meeting of the participants during the first year, and will have some more travelling than the other participants to be able to visit all participating laboratories.

In addition to the contractors listed in part 1, some organizations are are collaborating on an informal basis:

The JRC Isptra, Italy (Dr. Serrini) will act as a full member of the group of participants. The JRC will not apply for reimbursement through the STEP project, as it has direct EC funding.

The University of East Anglia, Great Britain (Dr. S. Penkett) will also act as a member of the group, although the degree of participation is presently not clearly stated. Dr. Penkett is already involved in other

110 PART 2 (continuation)

FOR COMMISSION USE

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DETAILED DESCRIPTION OF THE PROPOSED PROJECT
(continuation)

Page 12 of 14

STEP proposals. His participation in the PAN intercalibration will be financed by national sources.

Dr. Schmitt of Meteorologieconsult GmbH (Federal Republic of Germany) has established a close but informal co-operation with the KFA Juelich (Dr. Rudolph).

9-COMPLEMENTARITY BETWEEN PARTICIPATING ORGANIZATIONS

The collaborating organizations have very similar tasks within the project. But they will utilize widely differing methods. The main benefit will be the intercomparison of results from these different methods between organizations situated at different parts of Europe. Advanced technology and practical know-how will be spread among the partici-pants, and a basis for later comparison of measurements will be established.

10-EXPECTED ACHIEVEMENTS

See section 4 (THE OBJECTIVES OF THE PROPOSED PROJECT).

11-RECENT PUBLICATIONS BY PROPOSERS

P. PERROS, N. TSALKANI & G. TOUPANCE
PAN MEASUREMENTS IN A FORESTED AREA (DONON), FRANCE.
ENVIRON. TECHNOL. LETTERS, 1988, VOL 9, 351-358.

N. TSALKANI, P. PERROS & G. TOUPANCE
CONTINUOUS ATMOSPHERIC MEASUREMENTS OF PEROXYACETYL NITRATE (PAN) IN A MEDITERRANEAN SITE (ATHENS) GREECE. ENVIRON. TECHNOL. LETTERS, 1988, VOL 9, 143-152.

N. TSALKANI, A. MELLOUKI, G. POULET, G. TOUPANCE & G. LE BRAS
RATE CONSTANT MEASUREMENT FOR THE REACTION OF OH AND WITH PEROXY-ACETYLNITRATE AT 298K. J. ATMOS. CHEM., 1988, VOL 7, 409-419.

N. TSALKANI & G. TOUPANCE
INFRARED ABSORPTIVITIES AND INTEGRATED BAND INTENSITIES FOR GASEOUS PEROXYACETYL NITRATE (PAN). ATMOS. ENVIRON., 1989, VOL 23, N° 1, 1849-1854.

DETAILED DESCRIPTION OF THE PROPOSED PROJECT
(continuation)

Nieboer, H. and Ham, J. van, 1976.
Peroxyacetylnitrate (PAN) in relation to ozone and some meteorological parameters at Delft in the Netherlands
Atmos. Environ., 10, pp. 115-120.

Meyer, G.M. and Nieboer, H., 1977.
Determination of Peroxybenzoyl nitrate (PBZN) in ambient air.
VDI-Berichte, 270 pp, 55-56.

Jansen, J. and Hollander, J.C.Th., 1981.
Metingen van peroxyacetylnitraat en peroxypropionylnitraat te Delft in 1989 (in Dutch).
TNO report G 1089, juli 1981.

Hollander J.C.Th. and Verhagen, H.L.M., 1985.
Calibration of a PAN-monitor at the UBA pilot station Schauinsland.
TNO report R 85/239, oktober 1985.

Hollander, J.C.Th. and Nielen M.W.F., 1987.
Feasibility studies tenax adsorption tybes.
TNO report R 87/22, February 1987.

Guicherit, R., (1978).
Photochemical smog formation in the Netherlands.
TNO, Delft, 1978.

B. Vierkorn-Rudolph, J. Rudolph and S. Diederich, Determination of PAN in unpolluted areas, Int.J.Environ. Anal.Chem., 20, 131-149, 1985

J. Rudolph, B. Vierkorn-Rudolph and F.X. Meixner, Large-Scale distribution of PAN, Results from STRATOZ flights, J.Geophys.-Re., 92, 6653-6661, 1987

K.P. Mueller and J. Rudolph, An automated technique for the measurement of PAN in ambient air at ppb and ppt levels, Int.-J.Environ.Anal.Chem., 37, 256-262, 1989

K.P. Mueller, J. Rudolph and K. Wohlfahrt, Measurement of PAN in the marine atmosphere, Proceedings of the "Fifth European Symposium on Physico-chemical Behavior of Atmospheric Pollutants", 25-28 September 1989, Varese, Italy, in press.

R. Schmitt, B. Schreiber and I. Levin, Effects of long-range transport on atmospheric constituents at the baseline station Tenerife (Canary Islands), J. Atmos. Chem., 7, 335-351, 1988

FOR COMMISSION USE

EN G1 105157 [ ][ ] [G] [ ][ ][ ][ ][ ][ ]

DETAILED DESCRIPTION OF THE PROPOSED PROJECT
(continuation)

Page 14 of 14

1. ~~N.Rou~~melis and S.Glavas, Decomposition of Peroxyacetyl Nitrate and Peroxypropionyl Nitrate during Gas Chromatographic Determination with a Wide-Bore Capillary and two Packed columns, Anal.Chem. 61, 00 (1989).

2. G.Mineshos, S.Glavas and U.Schurath, Reactions of Peroxyacetyl Radicals with Sulfur Compounds, presented at the 5th European Symposium on Physico-Chemical Behaviour of Air Pollutants, Varese Sept. 1989.

3. E.Tsani-Bazaka, S.Glavas and H.Güsten, Peroxyacetyl Nitrate (PAN) Concentrations in Athens, Greece, Atmos.Environ. 22, 2283 (1988).

4. S.Glavas and U.Schurath, Peroxyacetyl Nitrate Forming Potential of Five Prototype Hydrocarbons, Environ.Sci. Technol. 19, 950 (1985).

5. S. Glavas and U.Schurath, Concentration and Storage of PAN for Mobile Field Measurements in Tropospheric Air, Chimica Chronika, New Series, 12, 89 (1983).

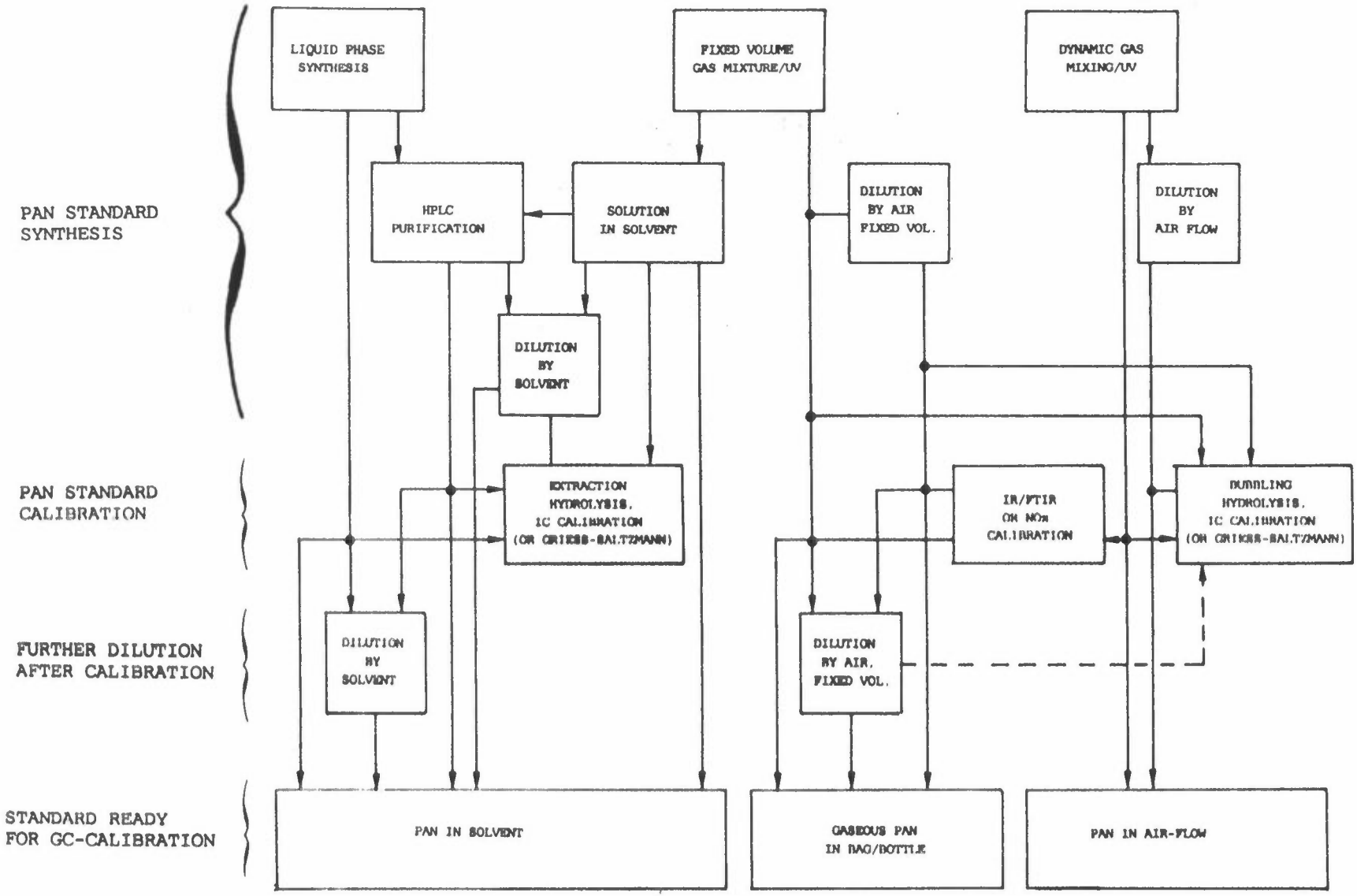

Figure 1. PAN standards may be produced and calibrated in many different ways, and may consequently have very different properties. The figure does not describe all possible combinations, but is intended to give an overview of the most frequently used principles. This figure describes the process of preparing a PAN standard, only. Also the calibration of a PAN instrument with the standard may be performed according to many widely differing methods.

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PARTICIPANT NUMBER 01 (as specified on page 2)

FOR COMMISSION USE
EN H1 105159 H

PART 3 - PARTICIPANT INFORMATION:

(to be completed by each participating organisation specified on page 2)

THE COORDINATOR X CR AC SC Linked to Contractor: (number specified on page 2 e.g. 01)

FULL LEGAL NAME OF ORGANISATION NORWEGIAN INSTITUTE FOR AIR RESEARCH

FULL ADRESS OF REGISTERED OFFICE (COMPANIES) OR PRINCIPAL OFFICE (OTHERS)

Street: No. BOX 64

Town: LILLESTROEM Posta Code 2001 CEDEX

Country: NORWAY Code NO Telephone 47 76814170 Ext:

Telex: Telefax 47 76819247

Teletext: E-Mail Type

ESTABLISHMENT, DEPARTMENT, DIVISION OR LABORATORY RESPONSIBLE FOR THE PROPOSED PROJECT:

ADDRESS IF DIFFERENT FROM ABOVE

Street: No.

Town: Posta Code CEDEX

Country: Code Telephone Ext:

Telex: Telefax

Teletext: E-Mail Type

FULL NAME OF PROPOSED PROJECT MANAGER (RESPONSIBLE SCIENTIST) MR TERJE KROGNES

POSITION: SCIENTIST

NATURE AND STRUCTURE OF ORGANISATION

Industry **Type:** Manufacturing Other (specify)

Size: BIG Small/Medium (SME)

No of employees < 20 20-99 100-499

University/higher education :

Research laboratory/institute : Private X State/Public Mixed

International organisation : **Other** (specify):

ATTENTION: Please — complete this form **accurately**; it will be used for **OPTICAL READING**
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PART 3 (continuation)

PARTICIPANT NUMBER 01

FOR COMMISSION USE

EN I1 105159 | | I | |

Is the participating organisation ultimately owned or controlled by another organisation? NO X YES

If YES, full legal name of owning or controlling organisation:

Country in which the owning or controlling organisation is situated:

In EC | | outside EC (specify) | | Code | |

Is the participating organisation affiliated to the coordinator, or any other contractor, associated contractor or major subcontractor in the proposed project? NO X YES

Where the participating organisation is an associated contractor or major subcontractor specify the name of the contractor to which it will be linked:

ESTIMATED BREAKDOWN OF COSTS

National currency (specify in words): NORWEGIAN CROWNS

Direct costs	NATIONAL CURRENCY	CURRENCY CODE	ECU	MAN-MONTHS
Labour	1872000	NOK	250000	24
Travel and subsistence	200000		26500	
Durable equipment	400000		53300	
Consumables	100000		13300	
External assistance				
Computing				
Other				
Indirect costs				
Overheads				
TOTAL	2572000		343000	

Basis of costs: full marginal

Financial contribution requested from EC (ECU) 170000 50 %

For participating organisations using marginal costs, specify the number of man-months of permanent staff effort to be devoted to the proposed project and not included in the marginal costs:

Academic/research | | Technicians | |

Others (specify) | | | |

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PART 3 (continuation)

PARTICIPANT NUMBER 6h

FOR COMMISSION USE

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USE OF RESULTS

FOREGROUND RESULTS

Are there any prior commitments or business interests of the participating organisation which:

(a) require it to divulge any information or results generated under the proposed project to any entity, other than another contractor or associated contractor in the project — NO [X] YES [ ]

If YES, specify name(s) of entity(ies) and nature of commitment:

(b) could affect the implementation of the proposed project or the availability of information or results generated under the project to others in accordance with the standard EC conditions for RTD contracts? — NO [X] YES [ ]

If YES, specify details of commitments or business interests

BACKGROUND RESULTS

List of patents held or information owned or controlled (background patents and information) by the participating organisation required for implementing the proposed project:

Patent number	Short description

Are there any restrictions relating to the disclosure or use of these patents or information in accordance with the standard EC conditions for RTD contracts?

— for RTD purposes: NO [ ] YES [ ]

— for exploitation or commercialisation: NO [ ] YES [ ]

If YES, specify details:

ATTENTION: Please complete this form **accurately**; it will be used for **OPTICAL READING** use typewriter set at **10 characters/inch** **Do not fold or staple** the form

PART 3 (continuation)

PARTICIPANT NUMBER 01

FOR COMMISSION USE

EN K1 105159 K

DETAILED DESCRIPTION OF THE CONTRIBUTION OF EACH PARTICIPANT

TO INCLUDE:

1 — the role and the contribution of the participating organisation,
2 — the experience of the participating organisation and of the project manager/responsible scientist (include on separate pages a list of a maximum of 5 recent relevant publications which best illustrate the competence of the project manager),
3 — the consistency of the proposed project with the corporate strategy of the participating organisation,
4 — the exploitation and dissemination policy relating to the results,
5 — any other relevant information to assist the EC,
6 — specific objectives and/or operational goals,
7 — work programme of the participant.

IMPORTANT

For optical reading and evaluation the information provided must be referenced by the numbers specified above.

1 - NILU will co-ordinate the proposed PAN intercalibration project. NILU will maintain contact with the Commission in Brussels and with the participants. NILU will prepare, calibrate and distribute PAN standards to the participants. NILU will set up a measurement site for PAN at its premises in Lillestroem, Norway, and equip this with a PAN analyzer and a PAN calibrator.

2 - NILU has for 20 years been dedicated to measurement and modelling of atmospheric pollution.NILU has worked with PAN measurement techniques since 1982. NILU has participated in several international intercalibration projects for various pollutants. Since 1986, NILU has constructed 6 PAN analyzers. One is installed at Spitsbergen and one in southern Norway. 4 instruments have been delivered to collaborating institutions in Sweden, Finland and Denmark. NILU has co-ordinated a small scale Nordic PAN intercalibration campaign (the results are due to be evaluated by spring 1990).

3- The proposed project is fully consistent with the corporate strategy of NILU.

4 - National measurement programmes will benefit from the improvements in PAN calibration techniques and data quality. NILU is furthermore in favour of communicating all relevant practical know-how between participants, and of publishing all results in reviewed journals.

5 -

We certify that the information set out in **Part 3** is correct and true and that we are authorised to participate in the proposed project.

	(authorised Scientific Official)	(authorised Administrative Official)
Name:	T. . KROGNES	H. . DOVLAND
Status:	SCIENTIST	DIRECTOR
Date:	28-12-1989	28-12-1989
Signature:	Terje Krognes	H Dovland

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118 PART 3 (continuation)

PARTICIPANT NUMBER 01

FOR COMMISSION USE

EN L1 105157 [ ][ ] [L][ ] [ ][ ][ ][ ][ ][ ]

DETAILED DESCRIPTION OF THE CONTRIBUTION OF EACH PARTICIPANT

(continuation)

6 - It is NILUs goal in the proposed project to establish a European platform for quality control of PAN calibrations.

7 - NILU has previously used a low concentration of PAN in hexane to prepare gaseous PAN samples in tedlar bags for PAN GC calibrations. NILU will construct a diffusion tube PAN calibrator and compare results from this to the tedlar bag technique. NILU will calibrate PAN standards with ion chromatographic analysis of Ac^- after bubbling and/or extraction hydrolization. NILU will furthermore co-ordinate the project, distribute PAN standards and edit internal reports as specified in part 2 of the proposal.

ATTENTION: Please — complete this form **accurately**; it will be used for **OPTICAL READING**
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ORIGINALS MUST BE USED

PARTICIPANT NUMBER 02 (as specified on page 2)

FOR COMMISSION USE

EN H1 102925 H

PART 3 - PARTICIPANT INFORMATION:

to be completed by each participating organisation specified on page 2)

THE COORDINATOR ☐ CR ☒ AC ☐ SC ☐ Linked to Contractor: (number specified on page 2 e.g. 01) ☐☐

FULL LEGAL NAME OF ORGANISATION UNIVERSITY PARIS XII

FULL ADRESS OF REGISTERED OFFICE (COMPANIES) OR PRINCIPAL OFFICE (OTHERS)

Street: No ☐☐☐ GENERAL DE GAULLE

Town: CRETEIL Postal Code: 94000 CEDEX 94010

Country: FRANCE Code FR Telephone 33148989144 Ext: 2495

Telex 264167F Telefax 33142077012

Teletext E-Mail Type

ESTABLISHMENT, DEPARTMENT, DIVISION OR LABORATORY RESPONSIBLE FOR THE PROPOSED PROJECT: LABORATOIRE DE PHYSICOCHIMIE DE L'ENVIRONNEMENT

ADDRESS IF DIFFERENT FROM ABOVE

Street: No

Town: Postal Code: CEDEX

Country: Code Telephone Ext:

Telex Telefax

Teletext E-Mail Type

FULL NAME OF PROPOSED PROJECT MANAGER (RESPONSIBLE SCIENTIST) G TOUPANCE

POSITION PROFESSOR

NATURE AND STRUCTURE OF ORGANISATION

Industry **Type:** Manufacturing ☐ Other (specify) ☐

Size: BIG ☐ Small/Medium (SME) ☐

No of employees < 20 ☐ 20-99 ☐ 100-499 ☐

University/higher education : ☒

Research laboratory/institute : Private ☐ State/Public ☐ Mixed ☐

International organisation : ☐ **Other** (specify): ☐

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PART 3 (continuation)

PARTICIPANT NUMBER 02

FOR COMMISSION USE

EN I1 102925

Is the participating organisation ultimately owned or controlled by another organisation? NO [X] YES [ ]

If YES, full legal name of owning or controlling organisation:

Country in which the owning or controlling organisation is situated:

In EC _____ outside EC (specify) _____ Code

Is the participating organisation affiliated to the coordinator, or any other contractor, associated contractor or major subcontractor in the proposed project? NO [X] YES [ ]

Where the participating organisation is an associated contractor or major subcontractor, specify the name of the contractor to which it will be linked:

ESTIMATED BREAKDOWN OF COSTS

National currency (specify in words): FRENCH FRANCS

	NATIONAL CURRENCY	CURRENCY CODE	ECU	MAN-MONTHS
Direct costs				
Labour	320000	FRF	40000	12
Travel and subsistence	100000		12500	
Durable equipment	240000		30000	
Consumables	60000		7500	
External assistance				
Computing				
Other				
Indirect costs				
Overheads	80000		10000	
TOTAL	800000		100000	

Basis of costs: full [ ] marginal [X]

Financial contribution requested from EC (ECU) 100000 100 %

For participating organisations using marginal costs, specify the number of man-months of permanent staff effort to be devoted to the proposed project and not included in the marginal costs:

Academic/research 6 Technicians [ ]

Others (specify) [ ]

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PART 3 (continuation)

PARTICIPANT NUMBER 02

FOR COMMISSION USE

EN J1 102925 | | J | |

USE OF RESULTS

FOREGROUND RESULTS

Are there any prior commitments or business interests of the participating organisation which:

(a) require it to divulge any information or results generated under the proposed project to any entity other than another contractor or associated contractor in the project — NO [X] YES [ ]

If YES, specify name(s) of entity(ies) and nature of commitment

(b) could affect the implementation of the proposed project or the availability of information or results generated under the project to others in accordance with the standard EC conditions for RTD contracts? — NO [X] YES [ ]

If YES, specify details of commitments or business interests

BACKGROUND RESULTS

List of patents held, or information owned or controlled, (background patents and information) by the participating organisation required for implementing the proposed project:

Patent number	Short description

Are there any restrictions relating to the disclosure or use of these patents or information in accordance with the standard EC conditions for RTD contracts?

— for RTD purposes: NO [X] YES [ ]

— for exploitation or commercialisation: NO [X] YES [ ]

If YES, specify details:

ATTENTION: Please complete this form **accurately**; it will be used for **OPTICAL READING** use typewriter set at **10 characters/inch** **Do not fold or staple** the form

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PART 3 (continuation)

PARTICIPANT NUMBER 02

FOR COMMISSION USE

EN K1 102925 | | | K | | | | | | |

DETAILED DESCRIPTION OF THE CONTRIBUTION OF EACH PARTICIPANT

TO INCLUDE:

1 — the role and the contribution of the participating organisation,
2 — the experience of the participating organisation and of the project manager/responsible scientist (include on separate pages a list of a maximum of 5 recent relevant publications which best illustrate the competence of the project manager),
3 — the consistency of the proposed project with the corporate strategy of the participating organisation,
4 — the exploitation and dissemination policy relating to the results,
5 — any other relevant information to assist the EC,
6 — specific objectives and/or operational goals,
7 — work programme of the participant.

IMPORTANT

For optical reading and evaluation the information provided must be referenced by the numbers specified above.

1 FULL MEMBER OF THE SET OF LABORATORIES WHICH WILL COMPARE THEIR COMPARE THEIR CALIBRATION TECHNIQUES FOR PAN
2 SEE ATTACHED SHEET (PUBLICATION LIST)
3 CLEAR
4 SEVERAL COOPERATIVE PUBLICATIONS IN INTERNATIONAL SCIENCE JOURNALS
5 ---
6 TESTING THE CONSISTENCY OF THE DIFFERENT POSSIBLE TECHNIQUES FOR CALIBRATING GC-ECD PAN ANALYSERS :
- IC OF ACETATES
- IR SPECTRA
- CHEMICAL ANALYSIS OF NITRITES (WEST-GAEKE)

7 WE WILL PARTICIPATE TO THE ANALYSIS OF SAMPLES OF PAN IN LIQUID HYDROCARBONS WHICH WILL BE MAILED BY NILU :
- CALIBRATION OF THE GC-ECD BY IR FROM THE TECHNIQUE AVAILABLE IN THE LAB
- ANALYSIS OF THE NILU SAMPLE BY THREE TECHNIQUES (INJECTION ON THE IR CALIBRATED GC-ECD, ANALYSIS BY WEST-GAEKE CHEMICAL METHOD, ANALYSIS BY IC OF ACETATES)
- COMPARISON OF THE RESULTS OBTAINED IN THE LAB AND BY OTHER LABS
- PARTICIPATION TO A FIELD INTERCOMPARISON CAMPAIGN : THE OBJECTIVE IS TO TEST IN REAL CONDITIONS, AND WITH SURE SIMILAR CONDITIONS OF CALIBRATION AND OPERATING CONDITIONS, THE WOLE ANALYTI CAL SYSTEM OF THE DIFFERENT TEAMS. PARTICIPATION TO A 2-3 DAYS SEMINAR ON PAN METROLOGY DURING THE CAMPAIGN.

We certify that the information set out in **Part 3** is correct and true and that we are authorised to participate in the proposed project.

	(authorised Scientific Official)	(authorised Administrative Official)
Name:	G. . TOUPANCE	D. . LAURENT
Status:	PROFESSOR	PRESIDENT Le Président de l'Université Paris Val-de-Marne
Date:	18/12/89	18/12/89
Signature:		Daniel LAURENT

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PARTICIPANT NUMBER 03 (as specified on page 2)

FOR COMMISSION USE
EN H1 105165 H

PART 3 - PARTICIPANT INFORMATION:

(to be completed by each participating organisation specified on page 2)

THE COORDINATOR ☐ CR ☒ AC ☐ SC ☐ Linked to Contractor: (number specified on page 2 e.g. 01) ☐

FULL LEGAL NAME OF ORGANISATION UNIVERSITY OF PATRAS

FULL ADRESS OF REGISTERED OFFICE (COMPANIES) OR PRINCIPAL OFFICE (OTHERS)

Street: No.

Town: PATRAS Postal Code 26110 CEDEX

Country: GREECE Code GR Telephone 3061993128 Ext:

Telex: 312447 UNPA Telefax 3061991996

Teletext: E-Mail Type

ESTABLISHMENT, DEPARTMENT, DIVISION OR LABORATORY RESPONSIBLE FOR THE PROPOSED PROJECT:

DEPARTMENT OF CHEMISTRY
SECTION OF ANALYTICAL,ENVIRONMENTAL AND APPLIED CHEMISTRY

ADDRESS IF DIFFERENT FROM ABOVE

Street: No.

Town: Postal Code CEDEX

Country: Code Telephone Ext:

Telex: Telefax

Teletext: E-Mail Type

FULL NAME OF PROPOSED PROJECT MANAGER (RESPONSIBLE SCIENTIST) DR SOTIRIOS GLAVAS

POSITION: ASSISTANT PROFESSOR

NATURE AND STRUCTURE OF ORGANISATION

Industry **Type:** Manufacturing ☐ Other (specify)

Size: BIG ☐ Small Medium (SME) ☐ No of employees < 20 ☐ 20-99 ☐ 100-499 ☐

University/higher education : ☒

Research laboratory/institute : Private ☐ State Public ☐ Mixed ☐

International organisation : ☐ **Other** (specify)

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PART 3 (continuation)

PARTICIPANT NUMBER 03

FOR COMMISSION USE

EN I1 105158 [ ] [I] [ ]

Is the participating organisation ultimately owned or controlled by another organisation? NO [X] YES [ ]

If YES, full legal name of owning or controlling organisation:

Country in which the owning or controlling organisation is situated:

In EC | outside EC (specify) | Code

Is the participating organisation affiliated to the coordinator, or any other contractor, associated contractor or major subcontractor in the proposed project? NO [X] YES [ ]

Where the participating organisation is an associated contractor or major subcontractor, specify the name of the contractor to which it will be linked:

ESTIMATED BREAKDOWN OF COSTS

National currency (specify in words): GREEK DRACHMAS

Direct costs	NATIONAL CURRENCY	CURRENCY CODE	ECU	MAN-MONTHS
Labour	5940000	GRD	33000	36
Travel and subsistence	1350000		7500	
Durable equipment	5400000		30000	
Consumables	5400000		30000	
External assistance				
Computing				
Other				
Indirect costs				
Overheads	4522000		25122	
TOTAL	22612000		125622	

Basis of costs: full [ ] marginal [X]

Financial contribution requested from EC (ECU): 125622 100 %

For participating organisations using marginal costs, specify the number of man-months of permanent staff effort to be devoted to the proposed project and not included in the marginal costs:

Academic/research 36 Technicians 1

Others (specify) 5 SECRETARY

ATTENTION: Please complete this form accurately; it will be used for OPTICAL READING use typewriter set at 10 characters/inch. Do not fold or staple the form

PART 3 (continuation)

PARTICIPANT NUMBER 03

FOR COMMISSION USE

EN J1 105165 | | J | |

USE OF RESULTS

FOREGROUND RESULTS

Are there any prior commitments or business interests of the participating organisation which

(a) require it to divulge any information or results generated under the proposed project to any entity, other than another contractor or associated contractor in the project — NO X YES ☐

If YES, specify name(s) of entity(ies) and nature of commitment

(b) could affect the implementation of the proposed project or the availability of information or results generated under the project to others in accordance with the standard EC conditions for RTD contracts? — NO X YES ☐

If YES, specify details of commitments or business interests

BACKGROUND RESULTS

List of patents held, or information owned or controlled, (background patents and information) by the participating organisation required for implementing the proposed project:

Patent number	Short description

Are there any restrictions relating to the disclosure or use of these patents or information in accordance with the standard EC conditions for RTD contracts?

— for RTD purposes: NO X YES ☐

— for exploitation or commercialisation: NO X YES ☐

If YES, specify details:

ATTENTION: Please — complete this form **accurately**; it will be used for **OPTICAL READING** — use typewriter set at **10 characters/inch** — **Do not fold or staple** the form

PART 3 (continuation)

PARTICIPANT NUMBER 03

FOR COMMISSION USE

EN K1 105158 | | K | | | | | | |

DETAILED DESCRIPTION OF THE CONTRIBUTION OF EACH PARTICIPANT

TO INCLUDE:

1 — the role and the contribution of the participating organisation,
2 — the experience of the participating organisation and of the project manager responsible scientist (include on separate pages a list of a maximum of 5 recent relevant publications which best illustrate the competence of the project manager),
3 — the consistency of the proposed project with the corporate strategy of the participating organisation,
4 — the exploitation and dissemination policy relating to the results,
5 — any other relevant information to assist the EC,
6 — specific objectives and/or operational goals,
7 — work programme of the participant.

IMPORTANT

For optical reading and evaluation the information provided must be referenced by the numbers specified above.

1- Full member of a number of European laboratories which intercompare their PAN calibration techniques.

2- See attached sheet.

3- Clear.

4- Publications in international scientific journals.

5- =

6- The work herewith proposed to be executed consists of two parts: An intercomparison of the PAN calibration techniques and measurements of ambient PAN.
In the intercomparison experiment we will employ the two methods that we are currently using for the callibration of our ECD used for the measurement of PAN. The first method is based on injecting simultaneously certain amounts of gaseous PAN, in a GC coupled with an NOx chemiluminescent detector via a Mo-converter, and in a GC equipped with the ECD that is to be calibrated. The detection limit of this home-made GC-NOx detector of 10 ppbv, allows the simultaneous injection of the same PAN sample to the GC/ECD and thus attaining its calibration. To calibrate the ECD at lower concentrations we extrapolate and assume that the ECD remains linear in the range 10 ppb to 0.05 ppb the lowest ambient concentration expected. The second method we will use the alkaline hydrolysis of gaseous PAN samples and measurement of nitrite/nitrate ions as well as acetate ions by Ion Chromatography.
No systematic continuous values for PAN exist for Patras. Given the location of the University campus, where the sampling site will be located, it is possible to determine PAN values downwind of the plume of the city as well as upwind. Thus we will be able to determine the PAN values produced in the city as well as,more or less, the mediterranean background values of PAN. For this purpose we will use the meteorological data of wind direction and speed measured on campus. In addition temperature and rela-

We certify that the information set out in **Part 3** is correct and true and that we are authorised to participate in the proposed project.

	(authorised Scientific Official)	(authorised Administrative Official)
Name:	D.R. SOTIRIOS GLAVAS	Name: D.R. IOANNIS PANARETOS
Status:	ASSISTANT PROFESSOR	Status: VICE RECTOR OF UNIVERSITY
Date:	15 DECEMBER 1989	Date: 15 DECEMBER 1989
Signature:	Sotirios Glavas	Signature:

ATTENTION: Please — complete this form **accurately**; it will be used for **OPTICAL READING** — use typewriter set at **10 characters/inch** — **Do not fold or staple** the form

PART 3 (continuation)

PARTICIPANT NUMBER 03

FOR COMMISSION USE

EN L1 105158 [ ] [L] [ ]

DETAILED DESCRIPTION OF THE CONTRIBUTION OF EACH PARTICIPANT

(continuation)

tive humidity will be available. All of the above data will be evaluated and correlated with the PAN data of the rest of the participants.

7- Work programme: For the first six to nine months we will make- receive additional orders and set up the instruments for automatic operation. The ambient air PAN measurements will be carried out on a 24 hour basis by GC/ECD and capillary columns, lasting until the end of the project. Simultaneously the ECD will be calibrated with the existing means as routinely now done. For the intercalibrations specific PAN samples prepared by NILU will be analyzed in our laboratory and returned to NILU. This procedure will be repeated as specified in the detailed description of the overall proposal. If a number of beureaucratic details can be arranged we will also participate in the field intercomparison campaign arranged by NILU.

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PARTICIPANT NUMBER 04 (as specified on page 2)

FOR COMMISSION USE

EN H1 102925 H

PART 3 - PARTICIPANT INFORMATION:

(to be completed by each participating organisation specified on page 2)

THE COORDINATOR ☐ CR ☒ AC ☐ SC ☐ Linked to Contractor: (number specified on page 2 e.g. 01) ☐☐

FULL LEGAL NAME OF ORGANISATION

NETHERLANDS ORGANIZATION FOR APPLIED SCIENTIFIC RESEARCH
TNO DIVISION OF TECHNOLOGY FOR SOCIETY

FULL ADRESS OF REGISTERED OFFICE (COMPANIES) OR PRINCIPAL OFFICE (OTHERS)

Street: No. 501 LAAN VAN WESTENENK

Town: APELDOORN Postal Code: 7334 DT CEDEX

Country: THE NETHERLANDS Code NL Telephone 3155493493 Ext:

Telex: 39395 TNOAP NL Telefax 3155419837

Teletext: E-Mail Type

ESTABLISHMENT, DEPARTMENT, DIVISION OR LABORATORY RESPONSIBLE FOR THE PROPOSED PROJECT:

TNO DIVISION OF TECHNOLOGY FOR SOCIETY
DEPARTMENT OF ENVIRONMENTAL CHEMISTRY

ADDRESS IF DIFFERENT FROM ABOVE

Street: No. 97 SCHOEMAKERSTRAAT

Town: DELFT Postal Code: 2628 VK CEDEX

Country: THE NETHERLANDS Code NL Telephone 3115696900 Ext:

Telex: 38071 ZPTNO NL Telefax 3115616812

Teletext: E-Mail Type

FULL NAME OF PROPOSED PROJECT MANAGER (RESPONSIBLE SCIENTIST) DRS J.C.TH. HOLLANDER

POSITION: SCIENTIST

NATURE AND STRUCTURE OF ORGANISATION

Industry **Type:** Manufacturing ☐ Other (specify) ☐

Size: BIG ☐ Small/Medium (SME) ☐ No of employees < 20 ☐ 20-99 ☐ 100-499 ☐

University/higher education : ☐

Research laboratory/institute : Private ☐ State/Public ☒ Mixed ☐

International organisation : ☐ **Other** (specify): ☐

ATTENTION: Please — complete this form **accurately**; it will be used for **OPTICAL READING**
— use typewriter set at **10 characters/inch** — **Do not fold or staple** the form

PART 3 (continuation)

PARTICIPANT NUMBER 04

FOR COMMISSION USE

EN I1 102925

Is the participating organisation ultimately owned or controlled by another organisation? NO X YES

If YES, full legal name of owning or controlling organisation:

Country in which the owning or controlling organisation is situated:

In EC | outside EC (specify) | Code

Is the participating organisation affiliated to the coordinator, or any other contractor, associated contractor or major subcontractor in the proposed project? NO X YES

Where the participating organisation is an associated contractor or major subcontractor, specify the name of the contractor to which it will be linked:

ESTIMATED BREAKDOWN OF COSTS

National currency (specify in words): DUTCH GUILDERS

Direct costs	NATIONAL CURRENCY	CURRENCY CODE	ECU	MAN-MONTHS
Labour	883000	NLG	166500	15
Travel and subsistence	30000		13000	
Durable equipment	35000		15000	
Consumables	25000		11000	
External assistance				
Computing	10000		4500	
Other				
Indirect costs				
Overheads				
TOTAL	483000		210000	

Basis of costs: full X marginal

Financial contribution requested from EC (ECU) 105000 50 %

For participating organisations using marginal costs, specify the number of man-months of permanent staff effort to be devoted to the proposed project and not included in the marginal costs:

Academic/research | Technicians

Others (specify)

ATTENTION: Please complete this form accurately; it will be used for OPTICAL READING use typewriter and at 10 characters/inch Do not fold or staple the form

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PART 3 (continuation)

PARTICIPANT NUMBER 04

FOR COMMISSION USE

EN J1 102925 | | J | |

USE OF RESULTS

FOREGROUND RESULTS

Are there any prior commitments or business interests of the participating organisation which:

(a) require it to divulge any information or results generated under the proposed project to any entity, other than another contractor or associated contractor in the project — NO [X] YES [ ]

If YES, specify name(s) of entity(ies) and nature of commitment

(b) could affect the implementation of the proposed project or the availability of information or results generated under the project to others in accordance with the standard EC conditions for RTD contracts? — NO [X] YES [ ]

If YES, specify details of commitments or business interests

BACKGROUND RESULTS

List of patents held, or information owned or controlled, (background patents and information) by the participating organisation required for implementing the proposed project:

Patent number	Short description

Are there any restrictions relating to the disclosure or use of these patents or information in accordance with the standard EC conditions for RTD contracts?

— for RTD purposes: NO [X] YES [ ]

— for exploitation or commercialisation: NO [X] YES [ ]

If YES, specify details:

ATTENTION: Please — complete this form **accurately**; it will be used for **OPTICAL READING**
— use typewriter set at **10 characters/inch** — **Do not fold or staple** the form

PART 3 (continuation)

PARTICIPANT NUMBER 04

FOR COMMISSION USE

EN K1 102925 | | | K | | | | | | |

DETAILED DESCRIPTION OF THE CONTRIBUTION OF EACH PARTICIPANT

TO INCLUDE:

1 — the role and the contribution of the participating organisation,
2 — the experience of the participating organisation and of the project manager/responsible scientist (include on separate pages a list of a maximum of 5 recent relevant publications which best illustrate the competence of the project manager),
3 — the consistency of the proposed project with the corporate strategy of the participating organisation,
4 — the exploitation and dissemination policy relating to the results,
5 — any other relevant information to assist the EC,
6 — specific objectives and/or operational goals,
7 — work programme of the participant.

IMPORTANT

For optical reading and evaluation the information provided must be referenced by the numbers specified above.

1. TNO will contribute by setting up PAN-measurements at a measurement site in the northern part of the Netherlands, which will be operative over the required period for at least one year. With southern winds this site is downwind of major industrial areas in the Netherlands, Belgium and the Federal Republic of Germany. With northern winds there are no upwind industrial areas. The station will then receive unpolluted clean (polar) air masses straight from the North Sea and Atlantic Ocean.
TNO will contribute to the proposed publications and act as an editor for one of these, to be agreed upon later on. TNO will participate in all intercalibration rounds planned with both ionchromatographic analyses after hydrolyses and FTIR-analyses before hydrolyses, on both distributed standards and standards prepared by TNO.
We will also participate in the field intercalibration and workshop to be organized in Rome.
2. For over a decade TNO has carried out continuous measurements of the PAN concentrations in ambient air.
Both gaseous standards in pressurized cylinders and liquid standards (PAN in octane solution) have been produced and used for calibration. Based on this experience TNO has been consulted by many laboratories in Europe on this subject.
TNO has participated in several BCR-projects (BCR: Community Bureau of Reference) on the production and certification of standard reference materials and the stability of these materials.
TNO is involved in several internal projects on the chemistry and transport of air pollutants in particular photooxidants.
3. TNO is carrying out several national and international research projects on long range transboundary air pollution, global atmospheric chemistry, tropospheric ozone research,

We certify that the information set out in **Part 3** is correct and true and that we are authorised to participate in the proposed project.

(authorised Scientific Official)		(authorised Administrative Official)	
Name:	DR. R. GUICHERIT	Name:	DRS. J. WEMMENHOVE
Status:	HEAD DEPARTMENT OF ENVIRONMENTAL CHEMISTRY	Status:	HEAD FINANCIAL DEPARTMENT
Date:	891215	Date:	891215
Signature:		Signature:	

ATTENTION: Please — complete this form **accurately**; it will be used for **OPTICAL READING**
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132 PART 3 (continuation)

PARTICIPANT NUMBER 04

FOR COMMISSION USE

EN L1 102925

DETAILED DESCRIPTION OF THE CONTRIBUTION OF EACH PARTICIPANT
(continuation)

Page 1 of 2

covering both experimental and theoretical aspects. PAN is a major parameter in all those studies.

4. The results of the studies will be made available to the scientific community by publication in international journals. Data will be available for exchange with other laboratories.
5. -
6. Development of a standard reference method for calibration of PAN-analyzers. Other methods may be designated as equivalent. Establishment of a good quality controlled data base of PAN concentrations on a European scale available for studies on the role of PAN in atmospheric chemistry, long range trans-boundary air pollution, photooxidants budget.
7. The workprogramme of TNO will follow the general programme as given by the coordinating organization (NILU) and comprises the following activities.

First year:

- Setting up continuous, fully automated, PAN monitoring at an existing air pollution measuring site, including automatic data acquisition and performance monitoring of the PAN analyser by a propylnitrate permeation tube.
- Preparation of ionchromatographic method for analyses of the hydrolysed PAN-standards, including the hydrolysis step. At each stage in the programme ion chromatography of acetate and nitrate/nitrite-ions will be applied together with FTIR-analysis of the liquid standards before hydrolysis. The latter method is presently in use.
- Trial intercomparison of standards distributed by the coordinating organization. At each intercalibration round in the programme identical analyses will be carried out on the distributed samples and liquid standards synthesized by TNO.
- The calibration of the PAN-analyser will be carried out with static dilutions of aliquotes of standards of both sources in a tedlar bag with clean air, with addition of NO_2 to improve stability and with shielding from light by a dark cover. The PAN-analyser will sample from the tedlar bag as under normal (ambient air) sampling.
- Reports will be prepared on the state of the art of the present practice and experience with TNO, the results of the IC-analyses as compared to FTIR and the results of the trial intercalibration of the distributed standards.

Second year

- Measurement of PAN, continuously, over the period of at least one year, including data reduction, validation, summary statistics and relation to meteorological data. The analyser will be calibrated quaterly. With three rounds of intercalibration planned in programme, two additional calibrations have to be carried out with TNO-standards only.
- Participation in three rounds of intercalibration including IC- and FTIR-analyses of liquid standards from two sources (NILU

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ORIGINALS MUST BE USED

PART 3 (continuation)

PARTICIPANT NUMBER 04

FOR COMMISSION USE

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DETAILED DESCRIPTION OF THE CONTRIBUTION OF EACH PARTICIPANT

(continuation)

and TNO) as described above, and calibration of the PAH analyses with the standards of both sources.
- Reports of the results of the calibration and intercalibrations (3x).

Third year
- Report on the results of one year PAH-measurements. including all additional data-analyses necessary for the joint publications.
- Participation in the field calibration and comparative measurements to be organized in Rome.
- Contribution to the joint reports and publications on the project.
- TNO will act as an editor for one of the publications planned, to be agreed upon later on.

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PARTICIPANT NUMBER 05 (as specified on page 2)

FOR COMMISSION USE

EN H1 105161 H

PART 3 - PARTICIPANT INFORMATION:

(to be completed by each participating organisation specified on page 2)

THE COORDINATOR ☐ CR ☒ AC ☐ SC ☐ Linked to Contractor: (number specified on page 2 e.g. 01) ☐

FULL LEGAL NAME OF ORGANISATION METEOROLOGIE CONSULT GMBH

FULL ADRESS OF REGISTERED OFFICE (COMPANIES) OR PRINCIPAL OFFICE (OTHERS)

Street: No. 47 AUF DER PLATT

Town: GLASHUETTEN Postal Code 6246 CEDEX ☐

Country: FED.REP.OF GERMANY Code DE Telephone 49617461240 Ext:

Telex: ☐ Telefax 49617461436

Teletext: ☐ E-Mail Type ☐

ESTABLISHMENT, DEPARTMENT, DIVISION OR LABORATORY RESPONSIBLE FOR THE PROPOSED PROJECT:

ADDRESS IF DIFFERENT FROM ABOVE

Street: No. ☐

Town: Postal Code CEDEX

Country: Code Telephone Ext:

Telex: Telefax

Teletext: E-Mail Type

FULL NAME OF PROPOSED PROJECT MANAGER (RESPONSIBLE SCIENTIST)

POSITION:

NATURE AND STRUCTURE OF ORGANISATION

Industry **Type:** Manufacturing ☐ Other (specify) ☐

Size: BIG ☐ Small/Medium (SME) ☐ No of employees < 20 ☐ 20-99 ☐ 100-499 ☐

University/higher education : ☐

Research laboratory/institute : Private ☒ State/Public ☐ Mixed ☐

International organisation : ☐ **Other** (specify): ☐

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PART 3 (continuation)

PARTICIPANT NUMBER 05

FOR COMMISSION USE

EN I1 105155 | | I | |

Is the participating organisation ultimately owned or controlled by another organisation? NO X YES ☐

If YES, full legal name of owning or controlling organisation:

Country in which the owning or controlling organisation is situated:

In EC | outside EC (specify) | Code

Is the participating organisation affiliated to the coordinator, or any other contractor, associated contractor or major subcontractor in the proposed project? NO X YES ☐

Where the participating organisation is an associated contractor or major subcontractor, specify the name of the contractor to which it will be linked:

ESTIMATED BREAKDOWN OF COSTS

National currency (specify in words): GERMAN MARKS

	NATIONAL CURRENCY	CURRENCY CODE	ECU	MAN-MONTHS
Direct costs				
Labour	292070	DEM	143877	37
Travel and subsistence	24000		11822	
Durable equipment	276400		136158	
Consumables	139999		64938	
External assistance				
Computing				
Other				
Indirect costs				
Overheads	219960		108354	
TOTAL	942430		464251	

Basis of costs: full X marginal ☐

Financial contribution requested from EC (ECU) 232000 50 %

For participating organisations using marginal costs, specify the number of man-months of permanent staff effort to be devoted to the proposed project and not included in the marginal costs:

Academic/research | Technicians

Others (specify)

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PART 3 (continuation)

PARTICIPANT NUMBER ns

FOR COMMISSION USE

EN J1 105161 [ ][ ] [J][ ] [ ][ ][ ][ ][ ][ ]

USE OF RESULTS

FOREGROUND RESULTS

Are there any prior commitments or business interests of the participating organisation which:

(a) require it to divulge any information or results generated under the proposed project to any entity, other than another contractor or associated contractor in the project — NO [X] YES [ ]

If YES, specify name(s) of entity(ies) and nature of commitment

(b) could affect the implementation of the proposed project or the availability of information or results generated under the project to others in accordance with the standard EC conditions for RTD contracts? — NO [X] YES [ ]

If YES, specify details of commitments or business interests

BACKGROUND RESULTS

List of patents held, or information owned or controlled (background patents and information) by the participating organisation required for implementing the proposed project

Patent number	Short description

Are there any restrictions relating to the disclosure or use of these patents or information in accordance with the standard EC conditions for RTD contracts?

— for RTD purposes: NO [ ] YES [ ]

— for exploitation or commercialisation: NO [ ] YES [ ]

If YES, specify details:

ATTENTION: Please — complete this form **accurately**; it will be used for **OPTICAL READING** use typewriter set at **10 characters/inch** **Do not fold or staple** the form

PART 3 (continuation)

PARTICIPANT NUMBER 05

FOR COMMISSION USE

EN K1 105161 K

DETAILED DESCRIPTION OF THE CONTRIBUTION OF EACH PARTICIPANT

TO INCLUDE:

1 — the role and the contribution of the participating organisation,
2 — the experience of the participating organisation and of the project manager/responsible scientist (include on separate pages a list of a maximum of 5 recent relevant publications which best illustrate the competence of the project manager),
3 — the consistency of the proposed project with the corporate strategy of the participating organisation,
4 — the exploitation and dissemination policy relating to the results,
5 — any other relevant information to assist the EC,
6 — specific objectives and/or operational goals,
7 — work programme of the participant.

IMPORTANT

For optical reading and evaluation the information provided must be referenced by the numbers specified above.

1 The proposed participation in the PAN intercalibration programm includes the PAN measuring and calibration techniques used by Meteoconsult in Glashuetten and the Institut fuer atmosphaerische Chemie in Juelich. The tests, measurements, calibrations and comparisons will be done primarily by Meteoconsult, but the instumentation, expertise and know-how existing in Juelich will be available for the intercalibration project. Also the scientific evaluation of the data and the planning of the details of the experimental work will be done in close cooperation between Juelich and Glashuetten.

The available instumentation for PAN measurements is: automated ECD-GC with detection limits about 5ppt without preconcentration and preconcentration techniques with liquid N2 or a cryostat (-80 C) for cooling of the preconcentration loop including a fully automated combination of preconcentration and ECD-GC for PAN measurements in the tropospheric background with detection limits of less than one ppt.

These instuments are used routinely for field measurements and are available only for part of the time for the intercomparison experiments. Since the schedule of the intercomparison is rather tight and necessitates that a PAN instument is nearly permanently available (at least for the one year calibration phase which includes ambient measurements) an additional instrument is needed. It is planned to copy the existing techniques and this instrument will be available solely for the intercomparison and calibration project. The other instruments will be available for

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We certify that the information set out in **Part 3** is correct and true and that we are authorised to participate in the proposed project.

	(authorised Scientific Official)	(authorised Administrative Official)
Name:	R. . SCHMITT	R. . SCHMITT
Status:	CHIEF SCIENTIST	CHIEF SCIENTIST
Date:	15/12/1989	15/12/1989
Signature:	R. Schmitt	R. Schmitt

138 PART 3 (continuation)

PARTICIPANT NUMBER UP

FOR COMMISSION USE

EN L1 105454 [ ][ ] [L][ ] [ ][ ][ ][ ][ ][ ]

DETAILED DESCRIPTION OF THE CONTRIBUTION OF EACH PARTICIPANT
(continuation)

restricted time periods and this will allow parallel operation of similar instruments both with and without a preconcentration step. From these parallel runs, both with calibration gases, ambient air and the distributed PAN solution a realistic evaluation of the performance of the instruments will be possible during the "calibration phase" of the project, prior to the "field intercalibration exercise". This is relevant for a realistic planning of the details of the field intercalibration. The available calibration techniques are: liquid injection of PAN in dilute solutions, a permeation system capable of generating PAN in the lower ppb and ppt range in calibration gases (moist and dry gases) and a photochemical reaction system for the defined production of PAN in the gase phase. There are several techniques available for the absolute calibration of the "PAN sources": hyrolysis in alcaline solution combined with the determination of acetate, nitrite and nitrate by ionchromatography or colorimetric techniques (only nitrite and nitrate by a modified Griess-Salzmann method) and chemolumineszenz techniques for NO2- (following thermal decomposition of PAN) or NOy- (total odd nitrogen by catalytic conversion to NO) measurements are most frequently used by the participant.

These various methods allow a variety of checks and cross checks of the different PAN calibration methods.

This contribution also includes measurements at a background station in Tenerife. The instrument stationed in Tenerife will be included in the intercalibrations and thus produce background data which can be compared with the results from rural, semi rural and urban areas.

2 - Most of the scientists involved in this proposal have several years of experience in atmospheric trace gas measurements including PAN measurements and calibration. This includes measurements at background stations as well as with airplane and shipboard instruments.

3 - PAN measurements are important parts of many of the scientific programms the participant is involved in. Since calibration and quality control is of extreme importance for meaningful results, the participation in an intercalibration exercise is highly important and fully consistent with the participants concepts for atmospheric trace component measurements.

4 - The results from the PAN intercalibration project and the relevant experience and know-how will be made available to the other participants. The reporting procedures outlined in the main proposal will be followed. The general policy

PART 3 (continuation)

PARTICIPANT NUMBER 05

FOR COMMISSION USE

EN L1 105454 [ ][ ] [L][ ] [ ][ ][ ][ ][ ][ ]

DETAILED DESCRIPTION OF THE CONTRIBUTION OF EACH PARTICIPANT
(continuation)

of the participant is to present all relevant scientific results at international meetings and to publish them in reviewed jounals.

6 - This contribution to the project aims at testing and evaluation of PAN measurements with the final goal to obtain measuring and calibration procedures which are reliable, reproducable and can be compared with other laboratories. Also a PAN calibration technique and standard which is "generally accepted" should be established. Field data from background (Tenerife) and semi rural site (Juelich) which are well calibrated and intercompared will be produced.

7 - The work programm follows the schedule outlined by NILU. During the various phases of the intercalibration programm the outlined measuring and calibration procedures will be used and compared with the distributed standards by several measuring techniques. As part of the preparation phases I and II an instrument (copied from already existing methods) will be built in order to have one instrument which is permanently available for the intercalibration project.

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PARTICIPANT NUMBER 06 (as specified on page 2)

FOR COMMISSION USE

EN H1 105157 H

PART 3 - PARTICIPANT INFORMATION:

(to be completed by each participating organisation specified on page 2)

THE COORDINATOR ☐ CR ☒ AC ☐ SC ☐ Linked to Contractor: (number specified on page 2 e.g. 01) ☐☐

FULL LEGAL NAME OF ORGANISATION

Swedish Environmental Protection Agency
Atmospheric Research Division - ARD

FULL ADRESS OF REGISTERED OFFICE (COMPANIES) OR PRINCIPAL OFFICE (OTHERS)

Street No. Studsvik

Town Nyköping Postal Code 611 82 CEDEX

Country Sweden Code SE Telephone 46 155 211 63 Ext.

Telex 64013 studs s Telefax 46 155 631 10

E-Mail Type

ESTABLISHMENT, DEPARTMENT, DIVISION OR LABORATORY RESPONSIBLE FOR THE PROPOSED PROJECT:

Atmospheric Research Division

ADDRESS IF DIFFERENT FROM ABOVE

Street No.

Town Postal Code CEDEX

Country Code Telephone Ext.

Telex Telefax

Telegram E-Mail Type

NAME OF THE PROPOSED PROJECT MANAGER / RESPONSIBLE SPOT LIST Mr P P Oyola

POSITION Head of the Division

NATURE AND STRUCTURE OF ORGANISATION

Industry Type: Manufacturing ☐ Other (specify)

Size: BIG ☐ Small/Medium (SME) ☐

No of employees <20 ☐ 20-99 ☐ 100 over ☐

University/higher education : ☐

Research laboratory/institute : Private ☐ State/Public ☒ Mixed ☐

International organisation : ☐ Other (specify)

ATTENTION: Please complete this form accurately. It will be read by OPTICAL READING equipment and 10 characters only. Do not fold or staple.

PART 3 (continuation)

PARTICIPANT NUMBER 06

FOR COMMISSION USE

EN I1 105156

Is the participating organisation ultimately owned or controlled by another organisation? NO [X] YES [ ]

If YES, full legal name of owning or controlling organisation:

Country in which the owning or controlling organisation is situated:

In EC | outside EC (specify) | Code

Is the participating organisation affiliated to the coordinator, or any other contractor, associated contractor or major subcontractor in the proposed project? NO [X] YES [ ]

Where the participating organisation is an associated contractor or major subcontractor, specify the name of the contractor to which it will be linked:

ESTIMATED BREAKDOWN OF COSTS

National currency (specify in words): Swedish crowns

Direct costs	NATIONAL CURRENCY	CURRENCY CODE	ECU	MAN-MONTHS
Labour	450 000	SEK	60 000	22
Travel and subsistence	100 000		13 335	
Durable equipment	450 000		60 000	
Consumables	100 000		13 335	
External assistance				
Computing	50 000		6700	
Other				
Indirect costs				
Overheads				
TOTAL	1150 000		153 370	

Basis of costs: full [x] marginal [ ]

Financial contribution requested from EC (ECU): 76 685 — 50 %

For participating organisations using marginal costs, specify the number of man-months of permanent staff effort to be devoted to the proposed project and not included in the marginal costs:

Academic/research [ ] Technicians [ ]

Others (specify) [ ]

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PART 3 (continuation)

PARTICIPANT NUMBER 06

FOR COMMISSION USE

EN J1 105156 [ ][ ] [J][ ] [ ][ ][ ][ ][ ][ ]

USE OF RESULTS

FOREGROUND RESULTS

Are there any prior commitments or business interests of the participating organisation which:

(a) require it to divulge any information or results generated under the proposed project to any entity, other than another contractor or associated contractor in the project NO [x] YES [ ]

If YES, specify name(s) of entity(ies) and nature of commitment

(b) could affect the implementation of the proposed project or the availability of information or results generated under the project to others in accordance with the standard EC conditions for RTD contracts? NO [x] YES [ ]

If YES, specify details of commitments or business interests

BACKGROUND RESULTS

List of patents held, or information owned or controlled, (background patents and information) by the participating organisation required for implementing the proposed project:

Patent number	Short description

Are there any restrictions relating to the disclosure or use of these patents or information in accordance with the standard EC conditions for RTD contracts?

— for RTD purposes: NO [x] YES [ ]

— for exploitation or commercialisation: NO [x] YES [ ]

If YES, specify details

use typewriter set at 10 characters/inch — Do not fold or staple the form

PART 3 (continuation)

PARTICIPANT NUMBER 06

FOR COMMISSION USE

EN K1 105156 K

DETAILED DESCRIPTION OF THE CONTRIBUTION OF EACH PARTICIPANT

TO INCLUDE:

1 — the role and the contribution of the participating organisation,
2 — the experience of the participating organisation and of the project manager/responsible scientist (include on separate pages a list of a maximum of 5 recent relevant publications which best illustrate the competence of the project manager),
3 — the consistency of the proposed project with the corporate strategy of the participating organisation,
4 — the exploitation and dissemination policy relating to the results,
5 — any other relevant information to assist the EC,
6 — specific objectives and/or operational goals,
7 — work programme of the participant.

IMPORTANT

For optical reading and evaluation the information provided must be referenced by the numbers specified above.

1-PAN is an exellent indicator (better than ozone) of photochemical activity in the troposphere. PAN has been used to detect long range transport of photochemical oxidants to Scandinavia (report to be published). The ARD contribution to this project will be the instalationof a PAN instrument at the station Aspvreten located in the central part of Sweden.
The ARD will participate in all intercalibration proposed by NILU with our calibration technique. PAN is converted to NO and detected simultaneous with a NO-chemiluminescent analyzer and as PAN with an EC-GC.
The ARD will participate in the field intercalibration and in the Rome workshop.
2-Since 1970 the ARD has carried out continous measurements of O3, SO2, NO2, aerosol etc and PAN since two years ago.
The ARD is considered a national and scandinavian reference calibration laboratory.
3-The ARD is participating in the National Environmental Monitoring Programme and in several international projects, for instance TOR-Tropospheric Ozone Research, EMEP-European Monitoring and Evaluation Programme, NMR-Nordic Council of Ministers-Working group on Air Pollution. PAN isincluded in two of those projects as an important parameter.
4-The results of the PAN measurements will be included in a PAN database at NILU and will be available to the scientific community.
5-
6-Development of an in-situ calibration technique for PAN analyzers .
7-The workprogramme of the ARD will follow the general programme as given by the coordination organization - NILU.

We certify that the information set out in Part 3 is correct and true and that we are authorised to participate in the proposed project.

(authorised Scientific Official)		(authorised Administrative Official)	
Name:	M.r. P P Oyola	Name:	B.O. Jansson
Status:	Head of the Division	Status:	Professor
Date:	Dec 27, 1989	Date:	Jan. 03 1990
Signature:		Signature:	

144 PART 3 (continuation)

PARTICIPANT NUMBER 06

FOR COMMISSION USE

EN L1 105156 [ ][ ] [L][ ] [ ][ ][ ][ ][ ][ ]

DETAILED DESCRIPTION OF THE CONTRIBUTION OF EACH PARTICIPANT

(continuation)

Sampling and analysis of the VOC with steel canister and cryo,traping GC-technique. P Oyola R Romero

-

Publications:

Nordic intercomparison of O3 and NO2 measurement techniques. H Areskoug, P Oyola.

Field intercomparison between conventional and remote sensing techniques for background monitoring of NO2, SO2 and O3. G Nyquist, P Oyola.

PARTICIPANT NUMBER 07 (as specified on page 2)

FOR COMMISSION USE
EN H1 105163 H

PART 3 - PARTICIPANT INFORMATION:
(to be completed by each participating organisation specified on page 2)

THE COORDINATOR ☐ CR ☒ AC ☐ SC ☐ Linked to Contractor: (number specified on page 2 e.g. 01) ☐☐

FULL LEGAL NAME OF ORGANISATION CONSIGLIO NAZIONALE DELLE RICERCHE

FULL ADRESS OF REGISTERED OFFICE (COMPANIES) OR PRINCIPAL OFFICE (OTHERS)

Street: No. 7 PIAZZALE ALDO MORO

Town: ROMA Postal Code: 00185 CEDEX:

Country: ITALIA Code IT Telephone 06/49931 Ext:

Telex: Telefax 06/4957241

Teletext: E-Mail Type:

ESTABLISHMENT, DEPARTMENT, DIVISION OR LABORATORY RESPONSIBLE FOR THE PROPOSED PROJECT: ISTITUTO SULL'INQUINAMENTO ATMOSFERICO

ADDRESS IF DIFFERENT FROM ABOVE

Street: No. VIA SALARIA KM 29,300

C.P. 10

Town: MONTEROTONDO STAZIONE Postal Code: 00016 CEDEX:

Country: ITALIA Code Telephone 06/9005349 Ext:

Telex: Telefax 06/9005849

Teletext: E-Mail Type:

FULL NAME OF PROPOSED PROJECT MANAGER (RESPONSIBLE SCIENTIST) PA CICCIOLI

POSITION: SENIOR RESEARCHER

NATURE AND STRUCTURE OF ORGANISATION

Industry **Type:** Manufacturing ☐ Other (specify) ☐

Size: BIG ☐ Small/Medium (SME) ☐ No of employees < 20 ☐ 20-99 ☐ 100-499 ☐

University/higher education : ☐

Research laboratory/institute : Private ☐ State/Public ☒ Mixed ☐

International organisation : ☐ **Other** (specify): ☐

ATTENTION: Please — complete this form **accurately**; it will be used for **OPTICAL READING**
— use typewriter set at **10 characters/inch** — **Do not fold or staple** the form

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PART 3 (continuation)

PARTICIPANT NUMBER 07

FOR COMMISSION USE

EN I1 105163

Is the participating organisation ultimately owned or controlled by another organisation? NO [X] YES [ ]

If YES, full legal name of owning or controlling organisation:

Country in which the owning or controlling organisation is situated:

In EC | outside EC (specify) | Code

Is the participating organisation affiliated to the coordinator, or any other contractor, associated contractor or major subcontractor in the proposed project? NO [X] YES [ ]

Where the participating organisation is an associated contractor or major subcontractor, specify the name of the contractor to which it will be linked:

ESTIMATED BREAKDOWN OF COSTS

National currency (specify in words): LIRE ITALIANE

	NATIONAL CURRENCY	CURRENCY CODE	ECU	MAN-MONTHS
Direct costs				
Labour	30.000.000	ITL	20000	18
Travel and subsistence	22.500.000		15000	
Durable equipment				
Consumables	52.500.000		35000	
External assistance				
Computing				
Other	2.250.000		1500	
Indirect costs				
Overheads	2.400.000		1600	
TOTAL	151.500.000		101000	

Basis of costs: full [ ] marginal [X]

Financial contribution requested from EC (ECU): 101000 100 %

For participating organisations using marginal costs, specify the number of man-months of permanent staff effort to be devoted to the proposed project and not included in the marginal costs:

Academic/research 36 Technicians 36

Others (specify)

ATTENTION: Please complete this form accurately; it will be used for OPTICAL READING
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PART 3 (continuation)

PARTICIPANT NUMBER 07

FOR COMMISSION USE

EN J1 105163 | | J | |

USE OF RESULTS

FOREGROUND RESULTS

Are there any prior commitments or business interests of the participating organisation which:

(a) require it to divulge any information or results generated under the proposed project to any entity, other than another contractor or associated contractor in the project — NO [X] YES [ ]

If YES, specify name(s) of entity(ies) and nature of commitment

(b) could affect the implementation of the proposed project or the availability of information or results generated under the project to others in accordance with the standard EC conditions for RTD contracts? — NO [X] YES [ ]

If YES, specify details of commitments or business interests

BACKGROUND RESULTS

List of patents held, or information owned or controlled, (background patents and information) by the participating organisation required for implementing the proposed project:

Patent number	Short description

Are there any restrictions relating to the disclosure or use of these patents or information in accordance with the standard EC conditions for RTD contracts?

— for RTD purposes: NO [X] YES [ ]

— for exploitation or commercialisation: NO [X] YES [ ]

If YES, specify details:

ATTENTION: Please complete this form **accurately**; it will be used for **OPTICAL READING** use typewriter set at **10 characters/inch** **Do not fold or staple** the form

148 PART 3 (continuation)

PARTICIPANT NUMBER 07

FOR COMMISSION USE

EN K1 105163 | | K | | | | | |

DETAILED DESCRIPTION OF THE CONTRIBUTION OF EACH PARTICIPANT

TO INCLUDE:

1 — the role and the contribution of the participating organisation,
2 — the experience of the participating organisation and of the project manager/responsible scientist (include on separate pages a list of a maximum of 5 recent relevant publications which best illustrate the competence of the project manager),
3 — the consistency of the proposed project with the corporate strategy of the participating organisation,
4 — the exploitation and dissemination policy relating to the results,
5 — any other relevant information to assist the EC,
6 — specific objectives and/or operational goals,
7 — work programme of the participant.

IMPORTANT

For optical reading and evaluation the information provided must be referenced by the numbers specified above.

During the consolidation phase (PREP. I), the contribution of our organization will be devoted to improve the present methodology for producing PAN, which is based on the reaction between Acetaldehyde and NO_2 in the gas phase. The method is also suitable for PPN preparation providing that propyonaldehyde is used instead of acetaldehyde. Quantitation of PAN is carried out by conversion of PAN into acetate and nitrite by alkaline hydrolysis carried out at the column outlet by eliminating the EC detector. Analyses will be carried out by Ion Chromatography with eluant suppression. At the same time PAN will be prepared in liquid solution (nonane) by reaction between HNO_3 and peracetic acid (40%).
During the second phase (PREP. II), a new field-generator for PAN will be developed. It will be based on the formation of PAN by UV irradiation of mixtures of NO_2 and trans-2-butene generated by permeation tubes. The use of permeation systems, containing nonane solutions of PAN, will be also exploited and tested. These methods will be campared with those previously adopted. During the third phase (PREP. III), the standards received by the originator will be analyzed and compared to those available in the laboratory. The report will be sent at NILU. During the calibration phase, the instrument will be run over the entire year and analyses of PAN standards solutions, provided by the originator, will performed and the instrument calibrated according to the procedures developed through the experience accumulated during the various steps (CAL I, CAL II e CAL III). During the third year our Institute will host the field intercomparison PAN exercise planned around March 1992. During that time, the Institute will provide assistance, calibration procedures and will host the partecipants and the meeting necessary to harmonize the Intercomparison Exercise and the partecipants. Similarly to previous years, a report to NILU will be sent together with quality control assurance. The experience of the organization in this field is assured by the fact that our Institute is the first in Italy that has performed PAN measurements since 1984 and has developed suitable instrumentation for its measurement. This capability has been tested in the field during the field intercomparison exercise on Nitric Acid and Nitrate Measurements.

We certify that the information set out in **Part 3** is correct and true and that we are authorised to participate in the proposed project.

	(authorised Scientific Official)	(authorised Administrative Official)
Name:	P. . CICCIOLI	I. . ALLEGRINI
Status:	SENIOR RESEARCHER	DIRECTOR
Date:	19891219	19891219
Signature:	Paolo Ciccioli	

ATTENTION: Please — complete this form **accurately**; it will be used for **OPTICAL READING** — use typewriter set at **10 characters/inch** — **Do not fold or staple** the form

PARTICIPANT NUMBER 08 (as specified on page 2)

FOR COMMISSION USE: EN H1 102925 H

PART 3 - PARTICIPANT INFORMATION:

(to be completed by each participating organisation specified on page 2)

THE COORDINATOR ☐ CR X AC ☐ SC ☐ Linked to Contractor: (number specified on page 2 e.g. 01) ☐

FULL LEGAL NAME OF ORGANISATION INSTITUTO DE SALUD CARLOS III

FULL ADRESS OF REGISTERED OFFICE (COMPANIES) OR PRINCIPAL OFFICE (OTHERS)

Street: No. ☐ CARRETERA DE MAJADAHONDA A POZUELO KM 2

MAJADAHONDA

Town: MADRID Postal Code: 28220 CEDEX ☐

Country: ESPAÑA Code ☐ Telephone 3416391711 Ext ☐

Telex: 47209 INSAN Telefax 3416380613

Teletext: ☐ E-Mail Type ☐

ESTABLISHMENT, DEPARTMENT, DIVISION OR LABORATORY RESPONSIBLE FOR THE PROPOSED PROJECT: CENTRO NACIONAL DE SANIDAD AMBIENTAL

ADDRESS IF DIFFERENT FROM ABOVE ☐

Street: No. ☐ ☐

Town: ☐ Postal Code: ☐ CEDEX ☐

Country: ☐ Code ☐ Telephone ☐ Ext ☐

Telex: ☐ Telefax ☐

Teletext: ☐ E-Mail Type ☐

FULL NAME OF PROPOSED PROJECT MANAGER (RESPONSIBLE SCIENTIST) ☐ ROSALIA FERNANDEZ PATIER

POSITION: HEAD OF DEPARTMENT OF ENVIRONMENTAL HEALTH

NATURE AND STRUCTURE OF ORGANISATION

Industry Type: Manufacturing ☐ Other (specify) ☐

Size: R+D ☐ Small/Medium (SME) ☐

No of employees: 1-19 ☐ 20-99 ☐ 100-499 ☐

University/higher education : ☐

Research laboratory/institute : Private ☐ State/Public X Mixed ☐

International organisation : ☐ Other (specify) ☐

ATTENTION: Page ... must be filled in accurately as it is used for the OFFICIAL STARTING of the Project (Commission Decision). Any inaccuracy may cause delay in the Project start.

150 **PART 3** (continuation)

PARTICIPANT NUMBER 08

FOR COMMISSION USE

EN I1 102925 I

Is the participating organisation ultimately owned or controlled by another organisation? NO X YES

If YES, full legal name of owning or controlling organisation:

Country in which the owning or controlling organisation is situated:

In EC Outside EC (specify) Code

Is the participating organisation affiliated to the coordinator, or any other contractor, associated contractor or major subcontractor in the proposed project? NO X YES

Where the participating organisation is an associated contractor or major subcontractor, specify the name of the contractor to which it will be linked:

ESTIMATED BREAKDOWN OF COSTS

	National currency (specify in words)		ECU	MAN MONTHS
Direct costs				
Labour	10000000	ESP		2
Travel and subsistence	3000000			
Durable equipment	5000000			
Consumables	2000000			
External assistance	2000000			
Computing	3000000			
Other	1000000			
Indirect costs				
Overheads	2000000			
TOTAL	28000000		215385	
Basis of costs:	X			
			107692	50

PART 3 (continuation)

PARTICIPANT NUMBER 08

FOR COMMISSION USE

EN J1 102925 [ ][ ] [J][ ] [ ][ ][ ][ ][ ][ ]

USE OF RESULTS

FOREGROUND RESULTS

Are there any prior commitments or business interests of the participating organisation which:

(a) require it to divulge any information or results generated under the proposed project to any entity, other than another contractor or associated contractor in the project — NO [X] YES [ ]

If YES, specify name(s) of entity(ies) and nature of commitment

(b) could affect the implementation of the proposed project or the availability of information or results generated under the project to others in accordance with the standard EC conditions for RTD contracts? — NO [X] YES [ ]

If YES, specify details of commitments or business interests

BACKGROUND RESULTS

List of patents held, or information owned or controlled, (background patents and information) by the participating organisation required for implementing the proposed project:

Patent number	Short description

Are there any restrictions relating to the disclosure or use of these patents or information in accordance with the standard EC conditions for RTD contracts?

— for RTD purposes: NO [ ] YES [ ]

— for exploitation or commercialisation: NO [ ] YES [ ]

If YES, specify details:

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152 PART 3 (continuation)

PARTICIPANT NUMBER 08

FOR COMMISSION USE

EN K1 102925 K

DETAILED DESCRIPTION OF THE CONTRIBUTION OF EACH PARTICIPANT

TO INCLUDE:

1 — the role and the contribution of the participating organisation,
2 — the experience of the participating organisation and of the project manager/responsible scientist (include on separate pages a list of a maximum of 5 recent relevant publications which best illustrate the competence of the project manager),
3 — the consistency of the proposed project with the corporate strategy of the participating organisation,
4 — the exploitation and dissemination policy relating to the results,
5 — any other relevant information to assist the EC,
6 — specific objectives and/or operational goals,
7 — work programme of the participant.

IMPORTANT

For optical reading and evaluation the information provided must be referenced by the numbers specified above.

1) The "Centro Nacional de sanidad Ambiental" (CNSA) is the Reference Laboratory for the Spanish Air Pollution Network and also the National Laoratory for the BAPMoN-EMEP Network and WHO-GEMS-AIR. Furthermore, it participates in other EC projects.
2) The Responsable Scientist has a 15 years experience in the studies of physico-chemical behaviour of air pollutants, and the Spanish expert in the air quality methods, (annexed recent publications).
3) The proposed project is in the lines of research carry out by CNSA. These lines are directed to investigate the precursors of oxidants in the atmosphere (NO, VOC) and the final products of the photo-chemical reactions of these compounds. Among these components, PAN determinations have a special interest for our country, principally due to the peculiar meteorological conditions of the Peninsula and the air transport of precursors and their consequent transformation. The first phase of this PAN evaluation has being started.
4) The obtained results will be applied to different kinds of exploitation and disemination.
4.1.- Testing and standardization of methodology of calibration of PAN.
4.2.- Intercalibration of PAN samplers.
4.3.- Knowledge of the levels of PAN concentrations in Spain and determination of the proccess of formation of PAN in field atmosphere.
4.4.- Evaluation of the PAN episodes and their possible correlation with O_3 episodes.
5) The above mentioned information information also can be useful for the European countries, and a better knowledge of the problem of photo oxidation of the atmosphere in Southern Europe.

We certify that the information set out in Part 3 is correct and true and that we are authorised to participate in the proposed project.

(authorised Scientific Official)		(authorised Administrative Official)	
Name:	Dr. JOAQUIN MARQUEZ	Name:	Dr. RAFAEL NAJERA
Status:	SUBD INVESTIGACION	Status:	DIRECTOR GENERAL
Date:	21 DECEMBER 1989	Date:	21 DECEMBER 1989
Signature:		Signature:	

PART 3 (continuation)

PARTICIPANT NUMBER 08

FOR COMMISSION USE

EN L1 102925 [ ] [L] [ ]

DETAILED DESCRIPTION OF THE CONTRIBUTION OF EACH PARTICIPANT

(continuation)

Page 1 of 2

6) One of the principal objects, is to get better quality of the measurements of PAN and determine their temporal and spatial evolutions.
7) The work programme will be stablished in coordination with the project-coordinator. On this way it will carried out different phases.
7.1.- Selection and standardization of methodology .
7.2.- Intercalibration programme.
7.3.- Field measurements.
7.4.- Evaluation and interpretation of the results.

154 PART 3 (continuation)

PARTICIPANT NUMBER 08

FOR COMMISSION USE

EN L1 102925 [ ][ ] [L][ ] [ ][ ][ ][ ][ ][ ]

DETAILED DESCRIPTION OF THE CONTRIBUTION OF EACH PARTICIPANT

(continuation)

Some publications of the project manager:

* De la Serna, J.; Fernandez Patier, R.; Perez Carles, F.; Garcia Sanchez, J. y Esteban Lefler, M. (1986): "Anionic composition in size fractionated aerosol". Proceedings of "Fourth European Symposium on physico-chemical behaviour of atmospheric pollutants". Stressa (Italia). Sept. 23-25. Commission of the European Comunities, 11.

* Fernandez Patier, R.; Esteban Lefler, M. y de la Serna, J. (1987): "Comparison between rural and urban atmospheric aerosols in Spain" presentado en el "EMEP workshop on data analysis and presentation", 15-17 Junio. Colonia, (RFA), pag. 193-206.

* Fernandez Patier, R.; Esteban Lefler, M.; de la Serna, J. y Diez Hernandez, P. (1988): "Washout ratios of atmospheric acidic components in the centre of Spain". Proceedings of a "Workshop on field measurements and their interpretation" "Physico-Chemical behaviour of atmospheric pollutants". Villefranche sur Mer (Francia). 3-4 Mayo. Commission of the European Communities. Ed. S. Beilke, J. MOrelli y G. Angeletti, 308-316.

* De la Serna, J.; Fernandez Patier, R.; Santamaria, J.; Fernandez San-Miguel, M.; Esteban Lefler, M; Diez Hernandez, P. y de Pablo Ricote, P. (1988): Physico-Chemical composition of the fog in a remote station in Spain". Presentado al 18th International Symposium of Environmental Analytical Chemistry y 4th International Congress on Analytical Techniques in Environmental Chemistry". Barcelona, 5-8 Sept.

* Fernandez Patier, R.; ESteban Lefler, M.; de la Serna, J. y Diez Hernandez P. (1989): "Field comparative study between atmospheric aerosol and precipitation in Spain". L.J. Brasser and W.C. Mulder (Eds.). Man and his Ecosystem. Proceedings of the 8th World Clean Air Congress. 1989. The Hague. Elsevier Science Publishers B.V. Amsterdan. 599-604.

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NORSK INSTITUTT FOR LUFTFORSKNING (NILU)
NORWEGIAN INSTITUTE FOR AIR RESEARCH
POSTBOKS 64, N-2001 LILLESTRØM

RAPPORTTYPE TEKNISK RAPPORT	RAPPORTNR. 7/90	ISBN-82-425-0152-1	
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TITTEL STEP PAN INTERCALIBRATION PREPARATIONS Project Planning Part 1	PROSJEKTLEDER T. Krognes
	NILU PROSJEKT NR. E-1000
FORFATTER(E) Terje Krognes	TILGJENGELIGHET * A
	OPPDRAGSGIVERS REF.

OPPDRAGSGIVER (NAVN OG ADRESSE)
NILU
Box 64
N-2001 LILLESTRØM

3 STIKKORD (a maks. 20 anslag)
PAN | INTERCALIBRATION | STEP

REFERAT (maks. 300 anslag, 7 linjer)

TITLE
STEP PAN INTERCALIBRATION, Project Planning Part 1

ABSTRACT (max. 300 characters, 7 lines)
A collection of documents concerning the planning of a PAN intercalibration project. Part 1 includes the project proposal to the EC STEP programme.

* Kategorier: Åpen - kan bestilles fra NILU A
Må bestilles gjennom oppdragsgiver B
Kan ikke utleveres C