

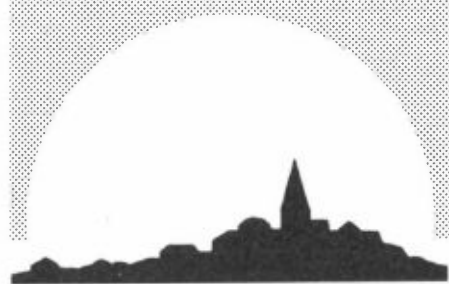
NILU TR: 5/91

NILU TR : 5/91
REFERENCE : O-91051
DATE : JUNE 1991
ISBN : 82-425-0258-7

PAN Measurement Technique Part 1

T. Krognes

*Experience gained at NILU in 1986-1987
Review of ECD theory*



NILU

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

CONTENTS

	Page
1 INTRODUCTION	3
2 MEASURING PRINCIPLE FOR PAN	4
2.1 The basic PAN instrument	4
2.2 The ECD (Electron Capture Detector)	5
2.3 PAN decomposition	8
3 PAN INSTRUMENTS USED AT NILU	11
3.1 The HARWELL instrument	11
3.2 The NILU instrument	12
3.3 The NILU-LAB instrument	12
3.4 The CARLO ERBA PAN ANALYZER	13
4 CONSIDERATIONS IN PAN INSTRUMENT CONSTRUCTION	14
4.1 Carrrier gas	14
4.2 Carrier gas bottle	15
4.3 Pressure regulator	16
4.4 Carrier gas filter	16
4.5 Needle valves and flow meters	17
4.6 Tubing and fittings	18
4.7 Sample intake	19
4.8 Sample valve	20
4.9 Sample loop	20
4.10 Column	21
4.11 Detector	23
4.12 Oven	23
5 INSTRUMENT ASSEMBLY	23
5.1 Leakages	24
5.2 Cleaning of parts	25
5.3 Cleaning of tools	27
6 SERVICING	27
7 A REVIEW OF THE ELECTRON CAPTURE DETECTOR	28
7.1 Detector geometry	28
7.2 Radioactive source	29
7.3 Carrier gas	30
7.4 Operation modus	31
7.4.1 Direct current	31
7.4.2 Pulsed mode, constant frequency	32
7.4.3 Pulsed mode, constant current	34
7.5 Operating parameters	34
7.5.1 Detector temperature	34
7.5.2 Carrier gas flow rate	36
7.5.3 Direct current excitation voltage	36
7.5.4 Pulsed mode, constant frequency	37

7.5.5	Pulsed mode, constant current	37
7.6	Electron capture detection models	39
7.7	Understanding PAN detection	42
8	ACKNOWLEDGEMENTS	43
9	REFERENCES	44

PAN MEASUREMENT TECHNIQUE, PART 1

1 INTRODUCTION

PAN is a widely used acronym for peroxyacetyl nitrate. The names peroxyacylnitrate or ethaneperoxoic nitric anhydride (EPNA) (Martinez, 1980) are also used. PAN is the first member of a homologous series of organic nitrogen compounds that are formed in the atmosphere by photochemical reactions (Eliassen, Hov, Isaksen, Saltbones and Stordal, 1982). (Stephens, 1969). PAN was first found in Los Angeles smog in 1956 (Stephens, Hanst, Doerr and Scott, 1956). In the early 1960s PAN was identified as an important constituent of smog-type photochemical air pollution. It is phytotoxic and an eye irritant (Darley, Kettner, Stephens, 1963). No stratospheric source of PAN has been known (Nieboer and Ham, 1975), PAN is therefore accepted as a better indicator of man-induced photochemical pollution than ozone. However, in a later work by Singh and Hanst (Singh and Hanst, 1981), a stratospheric source has been proposed. Based on the distribution of ethane and propane in the unpolluted atmosphere, Singh and Hanst predicted background PAN concentrations of 17 ppt in the lower troposphere, 90-360 ppt in the upper troposphere and 85 ppt in the lower stratosphere.

PAN is thermally unstable, at 20°C it has a half life of approximately 1 hour (Eliassen et al., 1982). At 0°C the half life is approximately 20 hours. It is therefore natural that PAN in Scandinavia is found both as a local pollutant and as a component in long-range transported pollution (Schjoldager, Dreiem, et al., 1983), (Schjoldger, Dreiem, et al., 1987), (Hoem, Dreiem, et al., 1988), (Ferm, Samuelsson, Sjødin, Grennfelt, 1984). In later years it has become increasingly evident that PAN is being transported into the arctic region and will be quite stable at the low temperatures there. PAN may therefore be an important factor in the arctic budget of organic nitrogen compounds (Penkett, Brice, 1986).

NILU has worked with measurement techniques for PAN since 1981. Systematic measurements of PAN have been performed by the Norwegian State Pollution Control authority (SFT) in Skien, southern Norway, in co-operation with NILU during several summer periods (Schjoldager, Dreiem, Wathne, Johannesen, Stige, Tveita, 1984), (Schjoldager, Dreiem, Krognnes, Johannesen, Stige, Tveita, 1987).

2 MEASURING PRINCIPLE FOR PAN

2.1 THE BASIC PAN INSTRUMENT

PAN is in most cases measured by a gas chromatograph equipped with a 6-port air sampling valve and a sample pump, a packed column and an ECD (Electron Capture Detector). The column is operated isothermally, in most cases between 30°C and 40°C. The stationary phase in most cases is Carbowax 400 or similar. The detector is operated at a temperature equal to the column temperature or up to about 70°C. The voltage output signal from the ECD controller may be registered on a strip chart recorder or directly processed by an electronic integrator. Such an instrument is essentially quite simple, but its operation and servicing requires some experience. Long-term automated operation in a remote location poses very exacting demands to the instrument construction.

To our knowledge, an adequate instrument is not commercially available. Carlo Erba has produced a prototype PAN instrument based on a commercial laboratory GC. NILU does not consider the reliability of this instrument adequate for unattended field operation. An operator must be present to restart the instrument after occasional hang-ups in the computer control system.

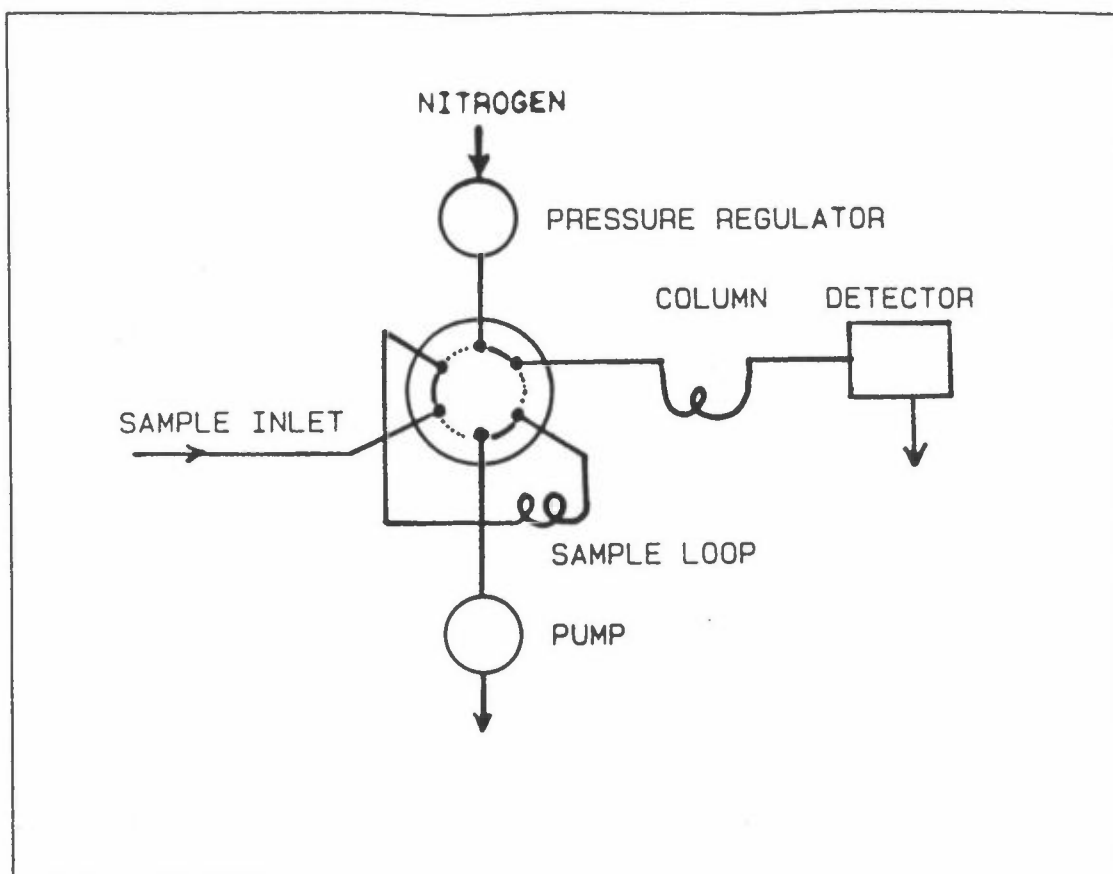


Figure 2.1.1: Basic PAN gas chromatograph. The instrument consists of a constant pressure carrier gas supply, a gas sampling valve, a packed column and an electron capture detector (ECD). The column and detector are usually maintained at a constant temperature between 30° C and 40° C.

The PAN instrument is dependent on a reliable calibration, as several loss and sensitivity factors may vary over time and between individual instruments. The methods for GC calibration and calibration of the standard itself are complicated. None of the "convenient methods" frequently described in the literature will make up for years of bitter experience.

2.2 THE ECD (ELECTRON CAPTURE DETECTOR)

Here a short introduction to the ECD is given. A review of ECD literature with emphasis on the requirements for PAN measurements, is given in a later chapter. The ECD is basically a chamber containing a source of free electrons (a radioactive foil emitting β^-). Carrier gas molecules are ionized by this radiation. A positive potential (constant or pulsed) is applied to an electrode within the chamber. The electrode will collect free electrons, producing a so-called "standing current" (baseline current). When an electron capturing compound enters the chamber, some electrons will be captured before they can be collected by the electrode. The current is thereby slightly reduced. This current reduction is converted to a positive voltage by a biasing network and an electrometer amplifier.

The ECD is usually operated at temperatures from 200°C to 300°C (in some cases up to 450°C). Only at these elevated temperatures will the metal surfaces of the electrodes be clean enough for reliable operation of the detector. At lower operating temperatures contaminants will accumulate on the electrodes. This will cause so-called contact potentials at the electrode surfaces. The contact potential polarity may be the same as that of the applied field, or it may oppose it. When high concentrations of reactive gases enter the detector, the contact potential will be affected, causing baseline level shifts. The baseline will be unstable and the detector properties may slowly drift for several days or weeks afterwards.

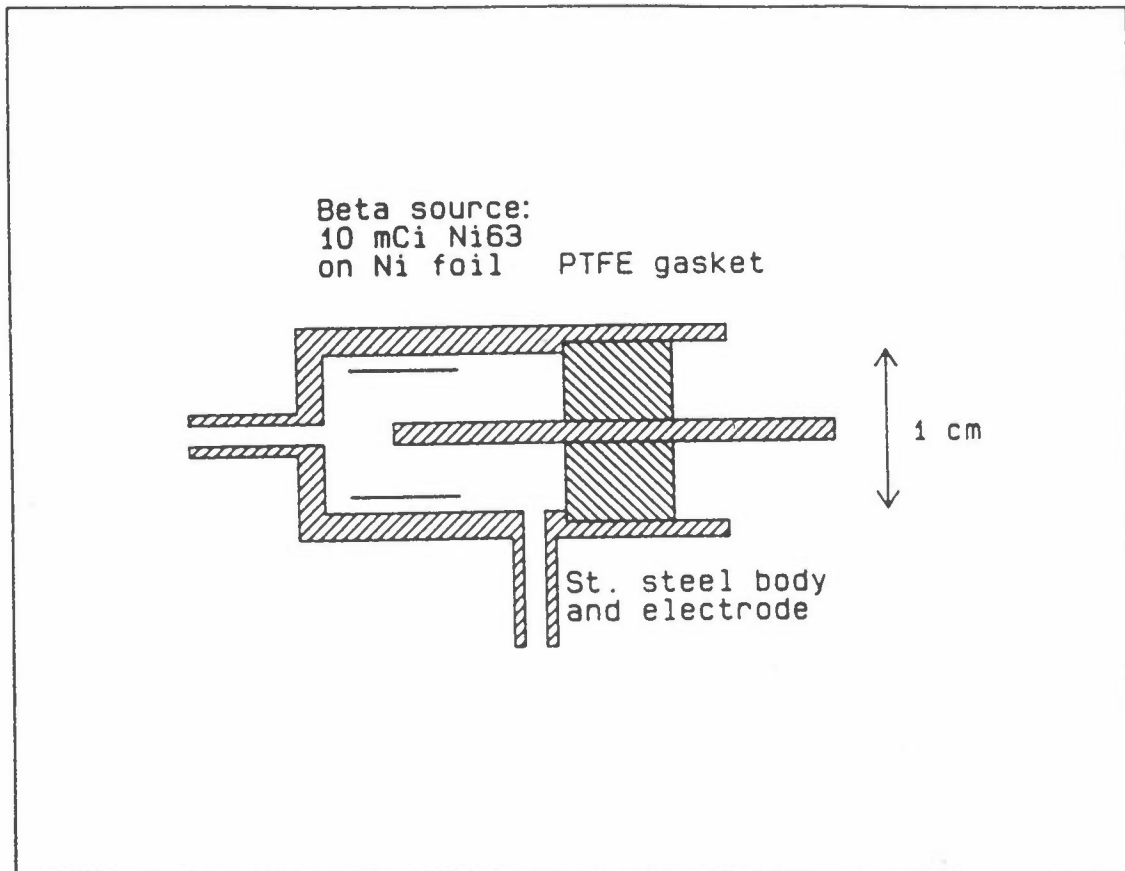


Figure 2.2.1: The simple ECD employed in several instruments used at NILU (Analytical Instruments Ltd. model 37210). The foil contains ^{63}Ni with an activity of 10 mCi. The geometry is cylindrical.

2.3 PAN DECOMPOSITION

In a PAN instrument the above mentioned problems can not entirely be avoided. PAN is thermally unstable. It decomposes quickly when coming into contact with metallic surfaces and when exposed to elevated temperatures. The main decomposition reaction can be described as follows:



The half life time of the PAN molecule is about 11 minutes at 30°C and about 3.6 minutes at 40°C (Eliassen et al., 1982). It is obvious that analysis time and temperature should be kept at the minimum level that will provide an adequate chromatographic separation. Otherwise a large percentage of the PAN in the sample will be lost before detection.

At 200°C the half life of PAN is expected to be about $3 \cdot 10^{-4}$ s. This makes it impossible to operate the detector at a temperature where contamination problems could easily have been avoided. Most workers in the field report operating their ECDs at temperatures from 30°C to 60°C. The ECD instability in this temperature range is one of the two main obstacles in the construction of a stable, reliable PAN instrument. The other main problem is loss of PAN to active surfaces in sample intake, valves and tubing.

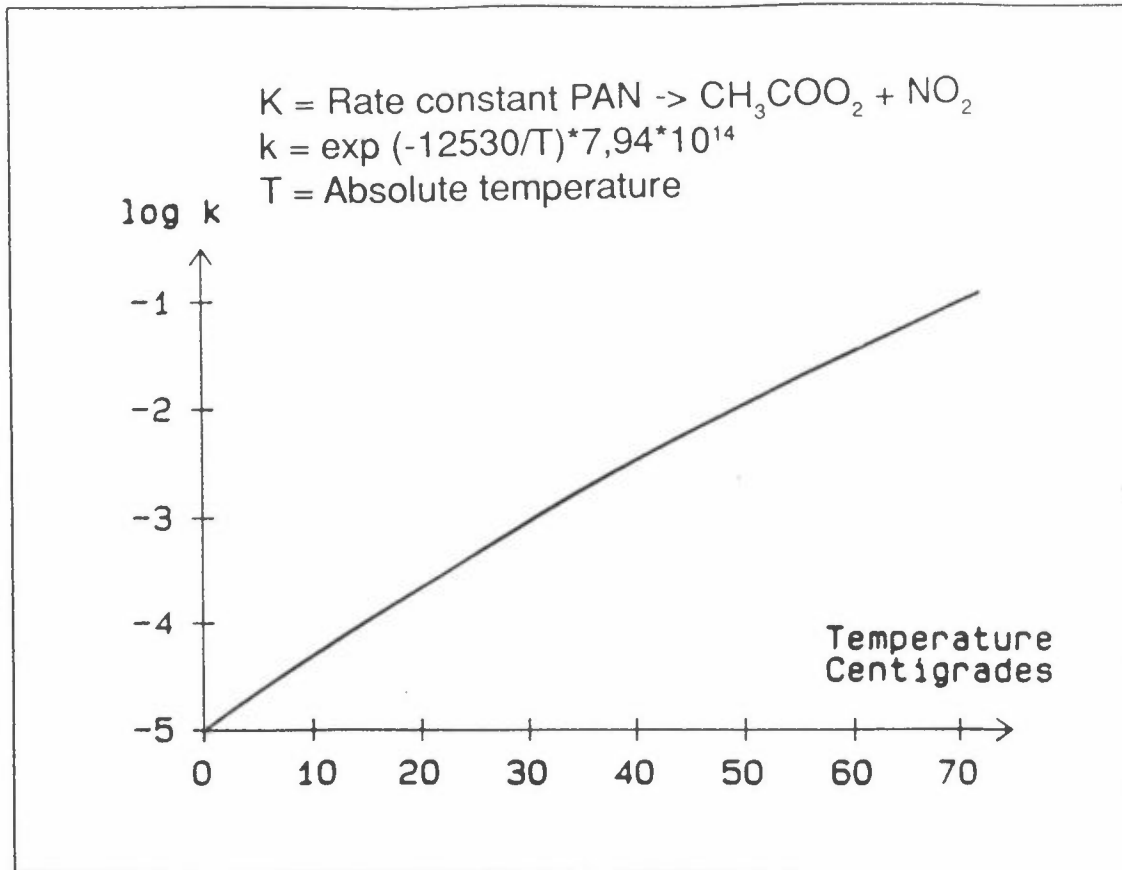


Figure 2.3.1: The rate constant k of the thermal PAN decomposition (Eliassen et al., 1982). The PAN loss with time may be computed from the formula:

$$C = C_0 * \exp(-kt)$$

Here C is the concentration of PAN at time t (in seconds), and C_0 is the concentration at time 0.

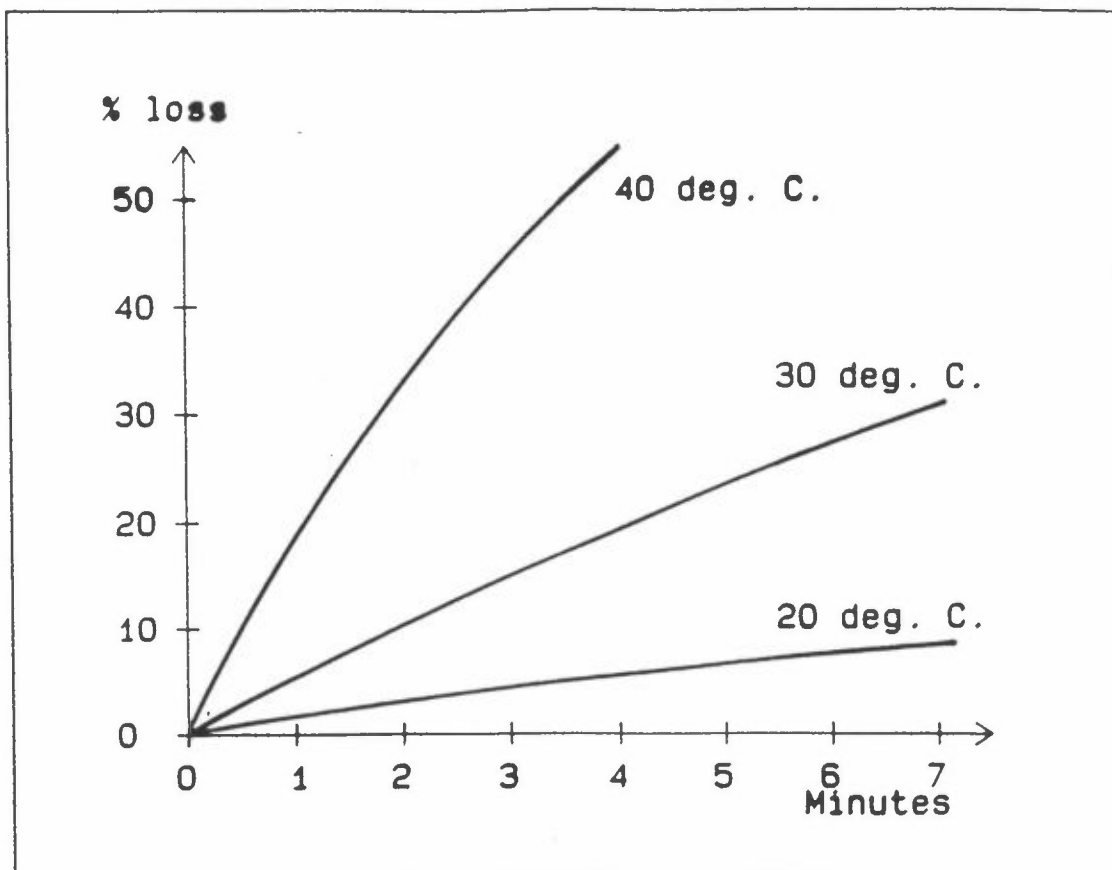


Figure 2.3.2: The theoretical thermal loss of PAN at different temperatures. When PAN is in the proximity of solid surfaces, the reaction products from PAN decomposition will take part in other reactions, and not be available for PAN re-formation. PAN will therefore be irreversibly lost after decomposition in GC sample intake or columns.

3 PAN INSTRUMENTS USED AT NILU

Several PAN instruments have been available to NILU. The following is a short description of each instrument.

3.1 THE HARWELL INSTRUMENT

This instrument was designed and built by Penkett and Brice at Harwell in 1980. It has later been extensively modified by NILU. As sample valve a Valco EC6P is now used. The instrument is equipped with two identical glass columns of 1 m length * 2 mm i.d. connected to a back-flush valve (Valco EC8P). The stationary phase is Chromosorb W-HP 80-100 mesh, coated with 5% Carbowax 400. The oven temperature is 35°C isothermal. The carrier gas is nitrogen at a flow rate of 47 ml/min. The carrier gas is purified in two Carlo Erba filter cartridges containing activated charcoal and molecular sieve 10 Å pre-treated at 300°C for 2 hours. The sample loop is made from 1/8" i.d. teflon tubing. A length of 2 m gives a volume of 4 ml. The sample pump is operated only 20 seconds before the sample injection.

The ECD (Analytical Instruments Ltd. model 37210) is a simple pin-cup construction operated at the column oven temperature. As ECD controller the original Harwell constant frequency oscillator and electrometer are still used. The pulse width is 2 μ s at a frequency of 4 kHz and 30 V amplitude. The standing current is typically 2.5 nA, depending on the contamination level.

The instrument is operated automatically by a SAIA PCA0 controller. Samples are taken every 15 minutes. Peak integration is performed by a Hewlett Packard 3390 Integrator.

This instrument has been used for most of NILUs routine PAN measurements. (The twin column backflush modification was installed in 1987.) The sensitivity is high, but can not be

exploited to its full potential due to baseline distortions when the instrument is contaminated.

3.2 THE NILU INSTRUMENT

This instrument was constructed by Mr. D. Brenna at NILU in 1983. It employs a Rheodyne PTFE 6-port sampling valve, an 80 cm by 4 m i.d. glass column packed with Chromosorb W 80-100 mesh coated with 5% Carbowax 400. The detector is identical to the one used in the Harwell instrument. The detector is operated in the constant frequency mode with 30 V pulse amplitude. The carrier gas is nitrogen at a flow of approximately 50 ml/min, filtered as described for the Harwell instrument above.

The instrument is automated by a built-in microcomputer. This computer initiates sampling at preprogrammed times, and it controls the sampling pump, the sampling valve and the oven temperature. The same computer also performs peak integration and calculates peak areas. A special feature is an automatic re-setting of the standing current (bias voltage) before each sample injection. By this technique a constant baseline level is achieved.

The sensitivity of this instrument was not as good as expected, and its long-term stability was not satisfactory. The instrument, however, provided valuable experience for further modifications of the PAN measurement technique.

3.3 THE NILU LAB INSTRUMENT

This is a laboratory set-up originally designed to test out various operation parameters. The instrument is operated manually. The sample valve is a Valco C6P. The separation column and the ECD are identical to those used in the Harwell instrument. Backflushing is not utilized.

The carrier gas is nitrogen purified by activated charcoal and molecular sieve at a flow rate of 30 ml/min. Column and detector are kept at 30°C.

The sample loop is made from 1/8" i.d. teflon tubing. A length of 1 m gives a volume of 2 ml. The sample pump is operated manually 15 seconds before injection.

A Carlo Erba Model 251 ECD controller running in the constant current mode is used. Pulse settings are 1 μ s pulse width and 30 V amplitude. The reference current is usually set to 0.8-1.1 nA. The attenuation is set to 32, and the signal is recorded on a strip chart recorder at 10 mV full scale deflection.

This instrument has been used to test different components and techniques in the laboratory. It has not been used for routine measurements.

3.4 THE CARLO ERBA PAN ANALYZER

This instrument consists of a modified VEGA GC 6000, a ICU 600 controller and an ECD 400 ECD controller. A 6 port stainless steel air actuated gas sampling valve and a sampling pump has been built into the GC. The sampling loop was made from stainless steel, and the volume was approximately 4 ml. The carrier gas was nitrogen purified in Carlo Erba stainless steel cartridges containing activated charcoal and molecular sieve 10 Å (the cartridges were external to the instrument). Carrier gas inlet pressure was set at 80 kPa and make-up at 50 kPa. The resulting flows were approximately 100 ml/min of carrier gas and 14 ml/min of make-up gas.

The ECD controller unit was operated at the original Carlo Erba settings: Constant current mode, pulse amplitude 25 V, pulse width 1 μ s, reference current 1.5 nA, and detector temperature 40°C (originally 60°C). Output attenuation was set to 32, and

the 10 mV output was connected to a strip chart recorder at 10 mV full scale deflection. During approximately 3 months of testing the reference current had to be gradually reduced to approximately 0.7 nA due to contamination build-up in the detector.

The instrument could not operate unattended over extended periods. After a power failure the instrument must be restarted manually by pressing the start button on the ICU 600 controller. During the test period the ICU 600 several times spontaneously entered the FORCED COOLING mode. An operator must place the instrument in STBY (stand-by) and wait 5 minutes before pressing the START button.

The instrument had excellent separation, but the PAN retention time of 8 minutes will cause some thermal PAN losses. The sensitivity for n-propyl nitrate (a stable compound otherwise quite similar to PAN) was excellent. The PAN sensitivity was much lower than could be accounted for by thermal losses. A contamination problem was suspected, but NILU returned the instrument without attempting to service it. Carlo Erba later informed NILU that before transport to NILU the original column had been broken and replaced with a column not previously tested for PAN.

4 CONSIDERATIONS IN PAN INSTRUMENT CONSTRUCTION

In the following sections the different components of the PAN instrument and their influence on the overall performance will be described in detail.

4.1 CARRIER GAS

Since the PAN instrument ECD is operated in a temperature range where it is very sensitive to contamination, a very pure carrier gas should be used. Grade 4.0 (99.99% N₂) is today the

only reasonably priced alternative in Norway. The producer specifies a "typical analysis" of contaminant concentrations: Ar < 1000 ppm, O₂ < 5 ppm, H₂O < 5 ppm and hydrocarbons < 5 ppm. At a substantially higher price, a "better grade" is offered. In most cases this gas comes from the same process and from the same storage tanks, it is only accompanied by an analysis certificate stating that this particular bottle is within the limits of the typical analysis.

5 ppm of unspecified hydrocarbons is a very large amount of unknown contaminants. Purification is therefore essential. It is also important to notice that many of these hydrocarbons condensate at elevated pressures. When the bottle pressure decreases, different contaminants will again evaporate and enter the carrier gas stream. Therefore only the largest bottles (50 litres, initial pressure 200-220 bar) should be used, and they should not be emptied below 50 bar before exchange.

4.2 CARRIER GAS BOTTLE

The shut-off valve on top of the bottle is lubricated, and it contains a polymer seal. The grease is probably of a good vacuum quality with a very low vapour pressure. But only a few molecules of it will be sufficient to disturb the ECD. Furthermore, the previous use of the bottle is always unknown, as bottles are circulated between users. A contaminated pressure regulator may have saturated the shut-off valve with contaminants. These contaminants may slowly be released into the carrier gas and into the chromatograph.

Special nitrogen bottles with dry, unlubricated valves are available. These are intended for medical purposes, and they are not circulated between users. However, the valves at the filling station are also lubricated, and the problems are probably not removed. To conclude, the instrument should be able to use a contaminated carrier gas, but the best quality gas and bottles that are easily available, should be used.

4.3 PRESSURE REGULATOR

A high quality two step regulator should be used. It is essential that it is a dry metal membran or metal bellows type made from stainless steel or brass. The pressure regulator will always become contaminated by oil residues from the gas bottle, but extra cleaning is normally not necessary, as the regulator is positioned before the carrier gas filter. Low quality lubricated pressure regulators must absolutely be avoided. No filter is capable of adsorbing the large quantities of contaminants they introduce into the system.

4.4 CARRIER GAS FILTER

The carrier gas should be purified by activated charcoal and molecular sieve (pore size 5 Å or 10 Å). The filter medium should be contained in a stainless steel cartridge with stainless steel frits serving as dust filters. A cartridge volume of 100 ml is sufficient for one 50 l nitrogen cylinder. Charcoal and molecular sieve may be contained in the same cartridge, or two cartridges may be used.

The molecular sieve must be activated (or regenerated) by heating to 300°C for a few hours or overnight under a gentle flow of nitrogen or helium (also this flow should be adequately purified). The charcoal must be renewed after use. If both agents are contained in the same cartridge, both charcoal and molecular sieve should be renewed when the filter is serviced.

O-ring seals are a notorious source of contaminants, and should be avoided. The filter cartridges should therefore be made from stainless steel tubing with stainless steel compression fittings serving as end caps.

One quite elegant filter system is called Gas-Clean (Chrom-pack). A prepacked pre-conditioned acrylic filter cartridge is mounted on a base plate. Valves automatically close the gas

lines when the filter cartridge is removed. Cartridges may therefore be exchanged with only small disturbances to the system. But the filter holder contains no less than 10 O-ring seals! These filters are very suitable for standard laboratory GCs equipped with high-temperature ECDs, but can not be recommended for PAN instruments. One of our PAN instruments was the victim of a serious contamination incident involving this filter system. A faulty O-ring opened a passage between a cavity in the filter holder and the inlet nitrogen flow. Over a period of approximately two years, the nitrogen deposited brown, sticky oil residues in this cavity. Then a leak developed in another O-ring on the outlet side. The contents of the cavity were injected directly into the GC, bypassing the filter cartridge. Not much of this reached the detector before the carrier gas supply was disconnected. But the detector needed several cleanings and a re-polishing of the centre electrode before it would again function at all. Its original performance has not been completely re-established (the teflon seal in the detector is not easily cleaned after such a disaster).

4.5 NEEDLE VALVES AND FLOW METERS

In ordinary laboratory gas chromatographs carrier and make-up gas flows are controlled by flow controllers, pressure regulators or needle valves. In some cases flow meters are connected to the inlet lines. All these components may contain O-ring seals, and therefore may be sources of contamination. Furthermore, they introduce complex geometries into the clean part of the flow system, and they are not easily cleanable after a contamination has occurred.

The flow control should therefore be restricted to the following elements:

- Constant inlet pressure is established by a high quality pressure regulator positioned before the carrier gas filter. A pressure meter may be connected to this regulator.

- Flow is restricted by the column itself or by a stainless steel restrictor (frit inserted into a union, or a short piece of SS tubing hammered flat). A stainless steel frit may be cleaned, a narrow tube section should be replaced if it becomes clogged. No adjustable flow restriction should be used.
- A flow meter or a flow controller may be placed after the outlet of the detector. No flow meter should be inserted anywhere else.

4.6 TUBING AND FITTINGS

Only SS (stainless steel) tubing should be used for carrier, make-up and sample gases. PTFE (teflon) tubing is suitable for sample transport to the chromatograph inlet and for the sampling loop. PTFE is porous, and oxygen will diffuse into any PTFE tubing. If 1 m of 1/8" PTFE tubing were included in the carrier gas line, the oxygen diffusing into the carrier gas would amount to 10-50 ppm. A similar oxygen contamination of the carrier gas would result from one pore of approximately 20 μ diameter in a metal tube wall. Furthermore, contaminants will always be present in the pores and cavities of PTFE, even if it is intrinsically clean and inert. The contaminants cannot be removed by any convenient form of cleaning or conditioning. They will continuously bleed into the carrier gas.

The oxygen contamination of the carrier gas is a more serious problem than the possible decomposition of PAN due to contact with metal surfaces. If the tubing is kept as short as possible and a small diameter (1/16") is used, the flow velocity will be high. Therefore, the time of contact between sample and metal tubing is too short to cause significant decomposition. To avoid adsorption at an active wall surface, only the best grade (preferably internally polished) of HPLC tubing should be used.

Only SS Swagelok or Valco compression fittings with SS ferrules should be used to connect SS tubing. Other brands of similar compression fittings will also serve, but brands should not be mixed, as they have slightly different geometries, and diffusion-tight connections are not always achieved.

Glass columns are connected to SS tubing with SS reducing unions (often a so-called zero dead volume bored through variety), using PTFE ferrules. This is one of the few places in the PAN instrument where PTFE cannot easily be avoided. Vespel ferrules are not as intrinsically clean or as inert as PTFE, but may possibly be used after thorough testing. Graphite ferrules may more easily leak due to cracks.

4.7 SAMPLE INTAKE

In some cases a continuously flushed sample intake is used. This will keep all surfaces in the intake in equilibrium with the sample air. In heavily polluted areas this method will, however, quickly coat the intake with different contaminants. Soot from car exhaust may create an excellent carbon filter in the intake tubing, adsorbing and destroying all PAN before it reaches the instrument. Airborne particles also may be deposited in the sampling valve, causing excessive wear, active surfaces, and leakages. Best results will be obtained with a short length of PTFE tubing taking the sample air directly from the outside or from a high volume (continuously vented) intake. The PAN instrument sample pump should only be operated 20-30 seconds before switching the sample valve.

A dust filter at the sample intake may be called for in very polluted environments. It is not recommendable in background areas. Such a filter must be thoroughly tested and found free of interferences and PAN adsorption. It would need to be frequently renewed. It is essential that all calibration samples are drawn through as much as possible of the intake system (especially including a dust filter). For this purpose the

intake construction should allow the intake tube and dust filter as one unit to be disconnected from the high volume intake or to be pulled in through the wall.

4.8 SAMPLE VALVE

To prevent the sample from coming into contact with metal surfaces, PTFE valves were first tested. They were however not found suitable. Virgin PTFE is mechanically too unstable to ensure reliable operation for more than a few weeks. Furthermore, dust entering the valve very quickly destroys the sealing surfaces, and leaks are unavoidable.

The teflon parts may be cleaned, but contaminants that have been absorbed cannot be completely removed.

Reliable operation was achieved with Valco P-series rotary valves. The rotor is made from carbon filled, compressed PTFE. The housing is highly polished stainless steel. The compressed teflon is virtually non-porous and very much more wear-resistant than virgin PTFE. After a year of continuous operation, traces of a black dust is seen in the column ends. This appears to come from the carbon filled PTFE rotor, but it does not seem to cause significant PAN losses. Valve leakages have not been found during this period.

4.9 SAMPLE LOOP

The sample will stay a few seconds in the sample loop before it is injected into the carrier gas stream. Therefore, to avoid decomposition, steel has in most cases not been used for the sample loop. Since the sample itself is air, oxygen diffusion is not a problem, and a suitable length of 1/8" PTFE tubing may be used. This is connected to short pieces of 1/16" SS tubing using SS reducing unions and SS ferrules. The 1/16" tubing connects directly to the Valco valve ports.

During the last year we have started using stainless steel sample loops without any significant increase in adsorption problems.

4.10 COLUMN

Traditional packed columns still give consistently better results in PAN analysis than wide-bore thick-film capillary columns. To prevent stationary phase bleeding from capillary columns, a bonding technique is used. The resulting stationary phase does not have a well defined melting point. Consequently the lowest operating temperature is not well defined. At the low operating temperatures and relatively high flow required for PAN analysis, excessive peak broadening occurs.

Columns made from PTFE or SS should be avoided for the reasons already mentioned above. Also glass-lined steel tubing is unsuitable since it is difficult to verify the quality of the very brittle glass lining.

Glass tubing remains the only material that can be recommended. It is non-porous, and it can be made very inert by pretreatment (silanizing). It is of course breakable, but the damage will be immediately obvious.

The stationary phase should be moderately polar to separate PAN from other compounds with similar boiling points. Short chain carbowax (CW400) or polyethyleneglycol (PEG400) are suitable. These compounds are liquids at room temperature, and have sufficiently low bleeding (low vapour pressure). In addition, these compounds do not contain electron capturing functional groups. The stationary phase is coated onto a high quality support material. A relatively thick layer of liquid phase (usually 5% by weight relative to the support) is used to improve the inertness of the column packing and to achieve the required separation. Only a highly inert support such as acid washed, silanized Chromosorb W-HP is suitable. In most cases

the particle size is 80-100 mesh or 100-120 mesh. The column must be properly packed according to good laboratory practise.

Occasionally a slow degradation of the coating may occur. This is indicated by an acrid smell after some months of storage. The packing material should in this case be discarded.

The column is plugged in both ends with silanized glass wool to prevent the packing material from spilling into tubing and valves. The glass wool has a very large surface area and therefore a large potential for adsorption of PAN or contamination of the system. The wool must be silanized. Shortly before use it must be conditioned at a high temperature. A suitable conditioning is 300°C for 2-4 hours under a clean nitrogen flow, at higher temperatures the silanizing will be destroyed.

The packed column must be conditioned before use. For at least 24 hours it should be kept at approximately 90°C under a gentle flow of purified nitrogen or helium. The temperature must not exceed 100°C, this could degrade or destroy the liquid phase.

Also the gas (helium or nitrogen) used for conditioning the column must be filtered as described above. The filter cartridge and tubing connections must be absolutely clean. The molecular sieve should be regenerated at 300-400°C for several hours immediately before column conditioning is started.

PAN is irreversibly adsorbed on a column which is not properly prepared. The silanization, coating and packing procedures must be carried out very carefully. If the conditioning procedures are not successfully performed, the baseline level will not stabilize. A sloping baseline will make it difficult for an electronic integrator to determine the beginning or the end of the PAN peak, thus reducing accuracy dramatically.

4.11 DETECTOR

Since the detector will be operated below 100°C, many of the sophisticated commercial designs that allow high temperature operation are useless. A simple design is adequate and perhaps preferable. For low temperature operation, PTFE seals may be utilized. They provide the best electrical insulation, and may easily be renewed when the detector is cleaned. In our laboratory we have continued to use the same simple detector type as was included in our first instrument. The benefit of using a component with well known properties has so far been more important than the possible refinements achievable with other detector designs.

The exhaust from the detector should be released through a few centimeters of narrow SS tubing. This prevents back diffusion of air into the detector.

4.12 OVEN

Normally the detector should be operated at a temperature 10 to 20 degrees above the column temperature to avoid contamination. At the low operating temperature used in a PAN instrument, the benefits of this precaution are small. In many cases both the column and the detector are therefore temperature regulated in the same oven. Only iso-thermal operation is required.

5 INSTRUMENT ASSEMBLY

The instrument should be assembled in such a manner that the flow system is known to be both clean and leak tight without any testing. It will in many cases be difficult to locate a leakage without contaminating the system. If one part was contaminated, the contamination will spread downstream, and first be observed when the detector itself has been contaminated. It is impossible to determine which part was

originally contaminated, so the whole system must be disassembled and cleaned. Therefore the carrier gas should never be connected until one is confident that the system is perfectly clean and leak tight. This approach is not as difficult as it may appear, but it requires systematic work.

5.1 LEAKAGES

There is a fundamental difference between a large and a small leak. In a large leak gas will flow, according to the laws of fluid mechanics, from the high pressure side to the low pressure side. This is the reason why a few centimetres of tubing is sufficient to prevent oxygen from entering the detector against the flow in the outlet. In a small leak there will be a molecular flow. Every single molecule is moving independently of all other molecules in the passage. The direction of the flow for each gas component is determined by the partial pressures on the inside and outside. Nitrogen will flow out of the system, but oxygen will flow into the system. The leakage will often depend on temperature, creating a temperature dependent baseline instability.

When new stainless steel compression fittings of small sizes (1/16" to 1/4") are correctly assembled and tightened (not overtightened!), they should not leak. Instructions accompanying every Swagelok fitting specify how much the nut should be turned for correct tensioning. For Valco nuts proper tensioning is not specified. Usually one half turn after finger tight is enough. It is essential to develop a feeling for just how much the fittings should be tightened. Every fitting should systematically be equally tightened.

A new Valco P-type valve may leak. The accompanying instructions describe how the valve should be cycled a few times to seat the rotor properly. If a leak is suspected, the rotor may be tensioned a bit more (1/4 turn of the nut) and again cycled a few times. The procedure may be repeated two or

three times. Normally the valve will now be leak tight. A leak detecting agent such as Snoop (Nupro Company) or similar should be used only as a last resort. Snoop has been used in our lab without contamination problems. It may be harmless at normal ECD operating temperatures, but at low operating temperatures it is a potentially serious contamination.

Brass fittings are more easily overtightened than SS fittings, and they also get more easily corroded. If possible, they should not be used. If a fitting suddenly "softens" during tightening, it should always be replaced. (It may not seem to be broken, but cracks have already developed!).

When the precautions mentioned above have been observed, the only spots that may possibly leak, are the PTFE ferrules in the column fittings and (if applicable) the PTFE seal in the detector. The column ends must be inspected carefully to reveal faults or cracks. 1/4" PTFE Swagelok ferrules will usually be leaktight when the nut is firmly finger tightened. Do not tighten too much at once. The PTFE will slowly give way until the connection is virtually free of stress. If a leak is suspected, tighten all PTFE ferrules a bit more (a small fraction of a turn). After a couple of repetitions the connections will be leak tight unless there are faults in the glass tube or foreign particles are stuck in the connection. The same procedure will do for a PTFE sealed detector. The seal will probably be more bulky than a set of ferrules, so a little more than finger tensioning may be required.

5.2 CLEANING OF PARTS

It is always difficult to determine whether a part should be cleaned or not. New, unused stainless steel tubing of pre-treated HPLC grade is usually clean enough to not contaminate the detector and dirty enough to not adsorb too much PAN. If it is too clean, the tubing will have a very active surface. This will be the case if the tubing has been heated to the point

where the surface water coating was removed. If solvents are used for cleaning, there is always a possibility that new contaminants are added by the solvent.

All fittings have been exposed to lubricants during machining. They should be cleaned in hexane + acetone + methanol in an ultrasonic bath for about 15 minutes. The solvents should be discarded and the procedure repeated three times. The fittings should then be dried under vacuum at 90°C for at least 12 hours. We also clean teflon ferrules with the same procedure, but use only methanol.

Valco valves may be disassembled and cleaned by the same procedure. The teflon parts may be cleaned with only methanol and ultrasonic sound. No metal object should be allowed to touch the sealing surfaces of rotor or housing. The polished steel surface is especially delicate. Damage occurs instantly at a light touch of any metal object. Extreme care must be taken during disassembling and reassembling.

If detector PTFE seals are cleaned, they should only be cleaned in methanol, and not be heated above 50°C during vacuum drying. At approximately 70°C any traces of acetone that might be present in the pores of the PTFE, will undergo pyrolyzation and destroy the electrical insulation properties of the PTFE. In some countries users are prohibited by law to open and service detectors containing a radioactive source. The low energy β -electrons are however quite harmless as long as the source foil is not touched by unprotected hands. Tweezers and strict laboratory cleanliness should be adequate.

The column should be flushed through with hexane and dried before packing. A glass wool stopper is inserted in one end of the column. This end is then connected to a small suction pump. The packing material is carefully poured into the column in small portions, and the column is carefully vibrated so that the packing material settles. A glass wool stopper is inserted

in the last 8-9 mm after the packing appears stable. The column should be conditioned as described above.

The carrier gas filter cartridge is included in the clean part of the flow system. The cartridge and its fittings should be cleaned by the same procedure as for other fittings.

5.3 CLEANING OF TOOLS

Any tools used for column packing and tube cutting should be cleaned using the same procedure as for the fittings. Where a tube enters a fitting, the tube end and two millimeters of the tube outside become internal surfaces in the flow system. Grease from bare hands will contaminate both tools and parts. Gloves should therefore be used during construction of the flow system. The work table should be covered with clean paper sheets.

6 SERVICING

As long as the instrument keeps running with a stable, sufficiently horizontal baseline, and with a constant sensitivity for both PAN and n-propyl nitrate, no servicing is required. Some preventive maintenance is nevertheless advisable. The carrier gas filter should be emptied, cleaned, refilled and reconditioned before contamination from the nitrogen cylinder breaks through. A six month interval seems reasonable.

When the standing current becomes too low, or the baseline stability too poor, the whole flow system should be dismantled and cleaned. The valve rotors and stators should be checked for wear and replaced if necessary. Cleaning of the parts and rebuilding of the instrument should be performed as described above.

7 A REVIEW OF THE ELECTRON CAPTURE DETECTOR

To understand the difficulties involved in performing accurate PAN measurements, a good understanding of the ECD is required. This review is deliberately focused on the qualitative aspects. For more quantitative information and mathematical treatises, please refer to the articles mentioned below. A good starting point for a more thorough study would be Aue and Kapila (Aue and Kapila, 1973), Pellizzari (Pellizzari, 1974), Zlatkis and Fenimore (Zlatkis and Fenimore, 1975) and Gobby, Grimsrud and Warden, 1980).

The ECD (Electron Capture Detector) was described by Lovelock in the early 1960s (Lovelock and Lipsky, 1960) (Lovelock, 1961). The detector consists of a reaction chamber irradiated by low energy free electrons from a radioactive source. The chromatograph carrier gas will be partially ionized by the bombardment, significantly increasing the number of free electrons in the chamber. When a voltage potential (constant or pulsed) is applied between two electrodes, the free electrons will be collected, and a small current (typically 0.5 to 5 nA) will flow through the detector. The accelerating potential is usually in the range 5 to 50 volts, the accelerated electrons should not reach an energy that could cause secondary ionization of the carrier gas.

When an electron capturing element or compound enters the detector chamber, the amount of free electrons in the chamber will be slightly reduced. This reduces the detector current. A high impedance biasing network and an electrometer amplifier will convert this to a positive voltage signal.

7.1 DETECTOR GEOMETRY

The early versions of the ECD were of the parallel plate variety. The electrodes were often the end walls of a cylindrical

chamber. The radioactive source was a foil positioned at one of the end walls.

The most commonly used geometry is the pin-cup ECD. A center electrode is positioned along the axis in a cylindrical chamber, the cylindrical wall constituting the other electrode. The radioactive source is a foil positioned along the cylindrical wall.

Several workers report improved performance achieved by the pin-cup geometry compared to the parallel plate geometry (Hartmann, Oaks, Dimick, 1967). Lovelock (Lovelock, 1968) explains that the geometry itself is not too important, but the dimensions are. All primary electrons from the β -source should be cooled down by the carrier gas. If these electrons are allowed to bombard the electrode directly, the detector will operate as a cross-section detector. In this case it will give positive peaks with compounds that do not have any affinity for free electrons, and it will be excessively sensitive to pressure and temperature changes. For this reason, a minimum distance must be maintained between the β -source and the electrode, the value of which depends on carrier gas and source type.

Several other geometries have been proposed. Aue and Siu (Aue and Siu, 1981) describe a two-chamber solution in which positive and negative ions are physically separated, thereby reducing the probability of recombination.

7.2 RADIOACTIVE SOURCE

The properties of several radiation sources have been described by Shoemaker, Fenimore and Zlatkis (Shoemaker, Fenimore and Zlatkis, 1965) and Hartmann, Oaks and Dimick (Hartmann, Oaks and Dimick, 1967), among several others. The two most commonly used isotopes in ECD are ^{63}Ni and ^3H (tritium). The most relevant physical properties are given in Table 1 below.

Hartmann, Oaks and Dimick report a somewhat higher sensitivity and greater linear range for an ECD with a ^3H source (when operated at 60-70 V constant voltage). Furthermore, the higher energy of the ^{63}Ni β - electrons calls for a larger detector diameter (and thereby a larger volume). Both these observations indicate that ^3H should be preferable. Tritium is a gas at standard conditions, it is bound to a stainless steel foil as titanium hydride (Ti^3H_2). It may be lost from the foil at excessive temperatures. ^{63}Ni source may safely be operated up to 400°C . At such elevated temperatures the detector becomes virtually immune to a large range of common contaminants. Ordinary tritium foils are usually limited to about 200°C . Ayaly and Wentworth (Ayaly and Wentworth, 1980) have reported detector performance with different sources, among these a scandium tritide foil (Sc^3H_3) that may be operated up to 325°C . The scandium tritide foil was also evaluated by Hartmann (Hartmann, 1973).

Dwight et al., (Dwight, Lorch and Lovelock, 1976) have suggested the use of Iron 55 as and Auger electron emitter. They report a significantly increased signal to noise ratio when comparing this source to commonly used sources.

Source	Energy MeV	Typ. activ. mCi	Optimum distance to electrode
^{63}Ni	0,067	10-15	6-8 mm (Lovelock, 1968: 10 mm)
^3H	0,018	20-200	2,5 mm
^{55}Fe	0,0055	5	-

7.3 CARRIER GAS

The carrier gas plays an active role in the operation of the ECD. Through repeated collisions it reduces the energy of the source electrons until they are in thermal equilibrium with the

gas. In elastic collisions between an electron and a monatomic gas "molecule" no kinetic energy is transferred. In inelastic collisions with more complex molecules the source electron will lose kinetic energy. The gas molecule may be excited in a vibrational or rotational mode, it may have an electron shifted into a higher energy orbital, or it may be ionized (lose an electron). Each primary electron from a β -source will ionize in the order of 100 to 1000 carrier gas molecules (Dwight, Lorch and Lovelock, 1976), (Gobby, Grimsrud and Warden, 1980).

Both nitrogen and argon are commonly used. Argon is usually mixed with 5% or 10% methane. Lovelock (Lovelock, 1963), (Lovelock, 1968) maintains that argon with 10% methane will give the most accurate results since it will cool down the primary electrons most efficiently and still allows electrons to have a high drift velocity. The methane quenching gas will through inelastic collisions dissipate the excess electron energy that is not expended by ionization of carrier gas molecules (Aue, Kapila, 1973). The quenching gas will also return excited carrier gas molecules to a normal state (Pellizzari, 1974). These could otherwise have destructed the sample molecules before electron capture could have taken place. Nitrogen, being a molecular gas, is capable of cooling down the source electrons to near thermal equilibrium without the addition of a separate quenching gas.

7.4 OPERATION MODUS

The way in which the excitation potential is applied to the detector causes large differences in performance. There are several different methods:

7.4.1 Direct current

When a constant voltage (DC) is applied to the detector, the free electrons in the detector chamber are continuously being

collected by the positive electrode. This was the original operation modus for the ECD.

Also molecular ions move in the electric field between the electrodes. They may contribute to the detector current, and they may build up a space charge opposing the field. The problems arising from this, and from other modes of detection than electron absorption, were described by Lovelock (Lovelock, 1963).

7.4.2 Pulsed mode, constant frequency

In the same paper (Lovelock, 1963) also described the pulsed mode operation of the ECD. The excitation potential is applied in short pulses (duration in the order of 1 μ s. Under these conditions, heavy molecular ions will not be much affected during the collection of free electrons. Space charge effects are therefore virtually eliminated. For most of the time there is no field applied, the free electrons will therefore be very close to thermal equilibrium with the carrier gas molecules. The concentration of free electrons will reach a maximum approximately 100 μ s after the pulse and remain at this level until the next pulse. Since a free electron is not immediately collected, it is allowed a much longer time to encounter an electron absorbing molecule. The detection efficiency is thereby increased. This mode of operation therefore offers increased sensitivity and increased accuracy compared to the DC mode.

The linear response range in the constant frequency pulsed mode is narrow. When an electron absorbing substance removes some of the free electrons, the detection efficiency will decrease. With pure carrier gas the detector supplies a standing current I_0 . When a small concentration of an electron absorbing substance enters the detector, the reduced detector current may be named I , and the instantaneous sample concentration, a , may be expressed by the formula:

$$I_0 - I = \text{const} * a \quad (1)$$

The detector is said to be saturated when I approaches zero. Another equation, valid for a larger dynamic range, was derived in 1966 (Wentworth, Chen and Lovelock, 1966):

$$\frac{I_0 - I}{I} = K * a \quad (2)$$

Here K is the electron capture coefficient for the sample substance. In 1968 an analogue converter was constructed to compute this function in real time (Fenimore, Zlatkis and Wentworth, 1968). The transformed signal could be applied to a conventional integrator or recorder. The group reported that equation (1) was valid only up to approximately 1% of saturation. By defining the lowest detectable signal as two times the detector noise level, the group calculated that the corresponding dynamic range was 250:1. The transformed signal was linear up to 90% of saturation. The corresponding linear dynamic range was 2.25×10^5 :1.

After redesigning the linearizing analogue converter, Fenimore and Davis presented additional results (Fenimore and Davis, 1970). Using a 30 mCi ^{63}Ni source, 30 ml/min argon /10% methane carrier, 1 μs pulse width, 20 V pulse height and a temperature of 200°C, they achieved linearity up to above 90% of saturation (with dissociative electron capture) at a pulse interval of 1000 μs . The linear range obtained is estimated to 1×10^5 :1. For shorter pulse intervals and for nondissociative electron capturing samples lower linear ranges were reported. (The terms dissociative and non-dissociative electron capture are treated in the section "Electron capture detection models" below).

7.4.3 Pulsed mode, constant current

The constant current mode was introduced in 1971 (Maggs, Joynes, Davies and Lovelock, 1971). The detector current is held constant by controlling the frequency of the voltage pulses. The linear relationship between frequency and sample concentration in the detector chamber is derived from Wentworth's model of the electron capture detection process (Wentworth, Chen and Lovelock, 1966). Using a 10mCi ^{63}Ni source, argon /5% methane carrier gas, a frequency range of 500 Hz to 500 kHz, 1 μs pulses of 60 V amplitude and a temperature of 200°C, they achieved a linear operating range of 5×10^4 and a detection limit of approximately 4×10^{-14} g/ml of dieldrin. The very stringent condition that the pulse interval should be 1000 μs or larger, does not apply to this mode of operation.

7.5 OPERATING PARAMETERS

When the detector type and geometry, the radioactive source, the carrier gas type and the detector operation modus are chosen, a number of additional parameters must be adjusted to optimize the method. These will be functions of the above mentioned choices, of the species to be measured, and of the required trade-off between sensitivity, linearity and long-term stability.

7.5.1 Detector temperature

The temperature should generally be slightly higher in the detector than in the column, which should again be slightly warmer than the carrier gas supply. This ensures that no component will condensate within the system.

The detection process is in most cases strongly temperature dependent. The type of electron attachment process that is involved in detecting the species, determines this dependency.

For a non-dissociative electron capturing species, sensitivity is highest at low temperatures (also refer to the section "Electron capture detection models below"). For a dissociative electron capture process sensitivity increases with increasing temperature. A high temperature may speed up decomposition of the sample so that a significant amount is lost before detection.

To keep detector contamination at a minimum, a high temperature is required. The electrodes will never be perfectly clean. A truly clean metal surface when exposed to the atmosphere will immediately be covered by a thin layer of water molecules. A variety of other compounds will stick to this water layer or directly to the metal surface. No form of cleaning can therefore produce a clean surface, it can only reduce the amount of unknown compounds in the surface coating. Some contaminants will adhere irreversibly to the surface (unless the detector is heated beyond normal operating temperature or cleaned chemically). For some contaminants there will be an equilibrium between the amount that sticks to the surface and the concentration of the same contaminants in the gas phase. A recently cleaned detector will therefore not necessarily be stable. The detector will be stable only if the contamination equilibrium can be maintained at a constant level.

The detector current is not only a function of the applied excitation voltage (and pulse width and pulse frequency). The compounds that are present in the surface layers will create surface potentials. Such potentials can add to or subtract from the excitation potential. If the contamination level is constant, the surface potentials may not cause any problems. If the contamination level changes slowly with time, detector sensitivity and baseline level will change accordingly. If there are large quick changes in the surface potentials, baseline instabilities will destroy the chromatograms.

In an air sample there will be large amounts of oxygen and water. These compounds will temporarily be added to the surface

layer, and may also react with the contaminants in the surface layer (also refer to Aue and Kapila, 1973). In both cases the contact potentials will be disturbed. The surfaces will then drift back to the equilibrium condition during a time period that may vary from a few seconds to 30 minutes or more. Also carrier gas flow and pressure changes affect the equilibrium of the detector.

Manufacturers design detectors with different geometries, different flow patterns, different materials etc. These factors will to some extent affect the time constant for variations in the contamination level. The only factor that significantly affects the level of the contamination equilibrium (and thereby the amplitude of the contact potential disturbances), is the operating temperature.

7.5.2 Carrier gas flow rate

A high carrier gas flow will help to flush contaminants out of the detector, unless the carrier gas itself is contaminated and poorly filtered (in very many cases it is!). A too high carrier gas flow (make-up gas included) will dilute the sample and reduce sensitivity. In some cases the detector will be mass sensitive, the response will then be independent of flow rate. If the detector operates as a concentration sensitive device, the product of peak area and flow rate will be proportional to the mass injected. In most cases optimum conditions must be found experimentally. Also refer to Devaux and Guiochon (Devaux and Guiochon, 1969).

7.5.3 Direct current excitation voltage

A low excitation voltage will not collect free electrons efficiently. Electron collection will also easily be prevented by contact potentials. A too high excitation voltage will cause excessive build-up of space charges by ion migration, and free

electrons will be accelerated to too high energies. Refer to Lovelock, (Lovelock, 1963), Devaux and Guiochon (Devaux and Guiochon, 1967), Landowne (Landowne, 1970), and Aue and Kapila (Aue and Kapila 1980).

7.5.4 Pulsed mode, constant frequency

Pulse width, pulse voltage and frequency should be optimized. Pulse width and voltage should be sufficient to collect all free electrons during a pulse. With nitrogen carrier gas this is achieved with approximately 2 μs at 30 V. With argon /5% methane corresponding results are achieved with a pulse width of approximately 0.5 μs and 30 V pulse height. A higher pulse voltage will reduce sensitivity to contact potentials. A too high pulse voltage may cause anomalous responses by accelerating free electrons to an energy where new ionizing collisions may take place. A high pulse frequency (pulse interval in the order of 100 μs) results in a high standing current, but sensitivity is reduced when the free electrons are not allowed sufficient time to react with the sample. Furthermore, maximizing linearity requires a pulse interval of 1000 μs or more. Also refer to Devaux and Guiochon (Devaux and Guiochon, 1967).

In this mode detector sensitivity is not affected by moderate changes in standing current. Contamination increase will reduce the number of free electrons in the detector chamber and change the surface contact potentials. This will only shift the baseline level. With heavy contamination the sensitivity and the linear operating range will be reduced.

7.5.5 Pulse mode, constant current

Modern ECD controllers tend to have only a few choices of rather short pulse widths (e.g. 1 μs and 0.1 μs). A large dynamic range requires a large frequency range, which in turn requires a short pulse width. At a high frequency and a wide

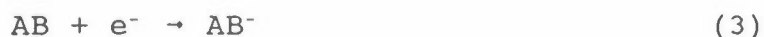
pulse width, linearity would be lost because operation is coming close to the direct current mode. Furthermore, sensitivity may actually be expected to increase if not all free electrons are collected in each pulse, as this increases the proportionality factor in the frequency to current relationship. Due to the same argument, increasing pulse voltage may in this mode reduce sensitivity. If all free electrons are collected during the pulse, an increased voltage will not affect sensitivity. Reducing pulse voltage will as before increase sensitivity to contact potentials.

When the pulse is too short to collect all free electrons in the chamber, only the electrons close to the collecting electrode will be collected. The detector becomes sensitive to the electron concentration only in a volume close to the electrode. If the sample elute is confined to the same volume (in a pin-cup geometry, make-up gas may flow along the outer cylindrical wall, and column elute in the central volume containing the center electrode), an increased signal to noise ratio may be achieved, but again at the cost of a lower linear range. What has effectively been done, is that the number of free electrons available for electron capture by the sample has been reduced.

A new operating parameter appears in this mode of operation. The constant current (often called the reference current) collected from the detector must be set between zero and the maximum current available. A low reference current results in a low baseline frequency, low sensitivity, large dynamic range and high long-term stability. Detector contamination will often increase slowly over weeks or months of continuous operation. The maximum available detector current will decrease. When the maximum available current comes close to the reference current, baseline frequency and sensitivity will both increase very much, and linear range will decrease. If the reference current is not set to a low value, long-term stability must be expected to be poorer in this mode of operation than in the constant frequency mode.

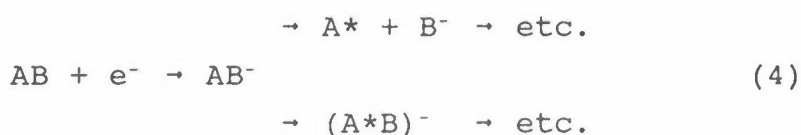
7.6 Electron capture detection models

In 1966 a theoretical model for the response of the pulsed electron capture detector was published (Wentworth, Chen and Lovelock, 1966). Practical measurements were shown to agree with the model. The paper examines the efficiency with which a short voltage pulse will collect the free electrons for various carrier gas compositions, pulse widths and pulse voltages. The two major types of electron attachment to an electron capturing species, AB, are described. In non-dissociative capture, the species AB forms a stable negative ion AB⁻:



In many cases the forward reaction will be only slightly temperature dependent, whereas the reverse reaction will increase with increasing temperature. The detection efficiency will then be decreasing with increasing temperature.

In dissociative electron capture the negative ion AB⁻ will immediately dissociate to form a radical and an ion, or to form a radical-ion.



These products may go through further reactions. In some cases some of the products may also be electron capturing. The dissociation will in most cases be quicker at higher temperatures, increasing detection efficiency with increasing temperature. In some cases dissociation will also be favoured by collision with electrons having a higher than thermal energy. In such cases a peak in sensitivity may be seen for a specific voltage in DC mode, and for a specific pulse voltage when the carrier gas is pure argon (which does not limit electron energy to thermal equilibrium by inelastic collisions). In that case the detector

is however not strictly operating as an electron capture detector.

Wentworths model is based on the following assumptions:

- The production of thermal electrons is a constant which is not affected by the presence of an electron capturing species.
- The reaction zone is assumed to be within the distance from the source that may be reached by the source electrons.
- The reaction zone has a large surplus of positive molecular ions, since these are only removed by the slow gas flow out of the cell, and by relatively infrequent recombination reactions. The electrons are quickly and repeatedly removed from the cell by the voltage pulses.
- The reaction zone is also assumed to have an excess of radicals, and to be homogeneous.
- The reaction zone is treated as a static system with respect to the electron concentration, since the flow out of the cell is very slow compared to the pulse intervals.

The different reactions that may create or remove free electrons and ions are formulated, and the rate of removal is expressed as a set of differential equations. A specific solution is found for the non-dissociative case:

$$\frac{b - [e^-]}{[e^-]} = K * a \quad (5)$$

Here b is the electron concentration when no electron capturing species is present in the chamber. The instantaneous electron concentrations is $[e^-]$. K is the electron capturing coefficient, and a is the instantaneous concentration of the electron capturing species. Observing that the detector current

is a function of the electron concentration at the moment the pulse is applied, the detector volume, and the pulse frequency, this relationship is transformed into equation (2) above.

It is seen that the detector generally responds to the concentration of the measured component. If the detector geometry and operating parameters allow the whole peak to be detected with a constant electron capturing coefficient (independent of the flow path through the detector and of the flow rate), the detector will respond to the mass of the component rather than the concentration. A particular case of this is the coulometric operation mode (may be achieved in both DC and pulsed operation modes). Here all sample molecules are detected, and detection efficiency is 100%. The response is now absolute. The number of sample molecules may be computed directly from the "missing current" without calibration experiments. In most cases the coulometric response appears for substances that undergo destructive detection with irreversible electron capture (Lovelock, Maggs and Adlard, 1971). Conditions for coulometric behaviour have been treated in numerous papers. Refer to Rosiek, Sliwka and Lasa (Rosiek, Sliwka and Lasa, 1977) and Broś and Page (Broś and Page, 1976).

The above theory by Wentworth et al., (often called a "stirred reactor" or "well mixed reactor" model) and derived theories rely upon the assumption that the free electrons play a dominating role in the ECD response mechanism. An alternative theory for the response mechanism has been developed by Gobby, Grimsrud and Warden (Gobby, Grimsrud and Warden, 1980). This theory incorporates electrostatic forces between charged particles. The most important aspects of the model were stated as follows:

- All thermal electrons are removed to the anode during the application of the pulse.
- The corresponding positive charge, created in the cell by electron removal, tends to dissipate itself by space-charge

driven migration to all grounded surfaces (including the anode) during the period between pulses.

- The thermal electrons produced throughout the cell during the period between pulses are concentrated in a localized zone of neutral charge (plasma). This zone is a cylindrical sheath positioned between the center electrode and the outer wall. Free electrons will immediately after their creation migrate to the zone of maximum positive potential, that is to the plasma region, which will grow with time until the next pulse.
- Positive ion density will be close to constant through the whole cell.

This model predicts that a fraction of the positive carrier gas ions will migrate to the center electrode and contribute to the measured current. The mathematical form of the response function is not changed, although the picture of the processes in the detector is quite different. In the cylindrical geometry the pulsed center electrode will receive the total current of free electrons and approximately 25% of the corresponding positive ions. The observed current is the difference between these two components.

7.7 Understanding PAN detection

The original Wentworth theory did not consider the fate of the ionized carrier gas molecules (positive ions). They were expected to be eventually flushed out of the detector by the carrier gas flow. The Gobby, Grimsrud and Warden theory consider the fate of both free electrons, positive ions and negative ions (sample molecules with captured electrons), and gives a wider understanding of the ECD.

The latter is a good basis for understanding the detection of PAN, but still much work remains. The ECD in a PAN instrument

is operated at a much lower temperature than the normal 200°C-300°C. The sample air introduces large amounts of oxygen and water vapour into the detector. A deep understanding of chemical and physical processes on the surface of the center electrode is needed to explain many aspects of the detector behaviour. The center electrode will have a surface layer of water, nitrogen ions, oxygen, and a number of unknown contaminants. The contact potential of this layer will influence the electrostatic conditions in the cell. The composition of the surface layer will be influenced by the sample and by pressure/flow transients. Any change that needs more time than the duration of a peak to return to an equilibrium, will cause detector instability. Such effects should be recognized in order to be avoided.

It may be possible to find an optimum detector temperature in the range from 50°C to 120°C (at the latter temperature the PAN half life will be approximately 70 ms, which is long compared to the pulse interval, but short compared to the total time a sample molecule will be inside the detector chamber). This optimum temperature must be expected to be unique for each detector and each combination of numerous other operating parameters. The existence of an optimum detector temperature higher than the column temperature has not really been established, as little is known about the electron attachment process for PAN or about the disintegration modes of the negative PAN ion (Ciccioli, Brancaleoni, Di Palo, Liberti, Di Palo, 1985).

8 ACKNOWLEDGEMENTS

The author wishes to thank Dr. M. Oehme, Mr. N. Schmidbauer and Mr. O. Hermansen of NILU for inspiration and insight, and for fruitful discussions and proof-reading. Also the secretaries at NILU have worked extra to finish this work.

9 REFERENCES

- Aue, W.A. and Kapila, S. (1973) The Electron Capture Detector - Controversies, Comments, and Chromatograms. J. Chrom. Sci., 11, 255-263.
- Aue, W.A. and Siu, K. W.M. (1981) A d.c. electron capture detector with separated ionization and capture regions. J. Chromatogr., 203, 237-244.
- Ayala, J.A. and Wentworth, W.E. (1980) Comparative investigation of radioactive sources for the electron capture detector. J. Chromatogr., 195, 1-15.
- Bros, E. and Page, F.M. (1976) Continuous stirred reactor model as basis for optimization of electron capture detector operation in coulometric and constant current modes. J. Chromatogr., 126, 271-277.
- Darley, E.F., Kettner, K.A., Stephens, E.R. (1963) Analysis of Peroxyacyl Nitrates by Gas Chromatography with Electron Capture Detection. Anal. Chem., 35, 589-591.
- Devaux, P. and Guiochen, G. (1967) The variations of the response factors of the electron capture detector with various parameters. J. Gas. Chrom., 7, 341-352.
- Devaux, P. and Guiochon, G. (1969) Variations of the response of the electron capture detector with carrier gas flow-rate. J. Chrom. Sci., 7, 561-564.
- Dwight, D.J., Lorch, E.A. and Lovelock, J.E. (1976) Iron-55 as an auger electron emitter, novel source for gas chromatography detectors. J. Chromatogr., 116, 257-261.
- Eliassen, A., Hov, Ø., Isaksen, I.S.A., Saltbones, J. and Stordal, F. (1982) A Lagrangian Long-Range Transport Model with Atmospheric Boundary Layer Chemistry. J. Appl. Met., 21, 1645-1661.
- Fenimore, D.C., Zlatkis, A. and Wentworth, W.E. (1968) Linearization of electron capture detector response by analog conversion. Anal. Chem., 40, 1594-1596.

- Fenimore, D.C. and Davis, C.M. (1970) Linear electron detection. J. Chrom. Sci., 8, 519-523.
- Ferm, M., Samuelsson, U., Sjödin, Å. and Grennfelt, P. (1984) Long-range transport of gaseous and particulate oxidized nitrogen compounds. Atm. Env., 18, 1731-1735.
- Gobby, P.L., Grimsrud, E.P., Warden, S.W. (1980) Improved Model of the Pulsed Electron Capture Detector. Anal. Chem., 52, 473-482.
- Hartmann, C.H., Oaks, D.M. and Dimick, K.P. (1967) Characteristics of the concentric tube and parallel plate electron capture detectors. Walnut Creek, CA., Varian Aerograph. (Technical bulletin 120-66).
- Hartmann, C.H. (1973) Evaluation of Tritiated Scandium for the Electron Capture Detector. Anal. Chem., 45, 733-739.
- Hoem, K., Dreiem, R., Krognes, T., Schjoldager, J., Stige, L., Tveita, B. (1988) Målinger av fotokjemiske oksidanter (ozon og PAN) i Norge 1986. Lillestrøm, (NILU OR 35/88).
- Lovelock, J.E. and Lipsky, S.R. (1960) Electron Affinity Spectroscopy - A New Method for the Identification of Functional Groups in Chemical Compounds Separated by Gas Chromatography. J. Am. Chem. Soc., 82, 431-433.
- Lovelock, J.E. (1961) Ionization methods for the analysis of gases and vapors. Anal. Chem., 33, 162-178.
- Lovelock, J.E. (1963) Electron absorption detectors and technique for use in quantitative and qualitative analysis by gas chromatography. Anal. Chem., 35, 474-481.
- Lovelock, J.E. (1968) Analysis by gas phase electron absorption. In: Internat. symp. on gas chromatography and its exploration. København 1968. Proc. Ed. by C.L.A. Harbourn and R. Stock. London, Institute of Petroleum. p. 95-108.
- Lovelock, J.E., Maggs, R.J. and Adlard, E.R. (1971) Gas-phase coulometry by thermal electron attachment. Anal. Chem., 43, 1962-1965.

- Maggs, R.J., Joynes, P.L., Davies, A.J. and Lovelock, J.E. (1971) The electron capture detector - a new mode of operation. Anal. Chem., 43, 1966-1971.
- Martinez, R.I. (1980) A Systematic Nomenclature for the "Peroxyacyl Nitrates", the Functional and Structural Misnomers for Anhydride Derivatives of Nitrogen Oxo Acids. Int. J. Chem. Kinet., 12, 771-775.
- Nieboer, H., van Ham, J. (1976) Peroxyacetyl Nitrate (PAN) in Relation to Ozone and some Meteorological Parameters at Delft in the Netherlands. Atm. Env., 10, 115-120.
- Pellizzari, E.D. (1974) Electron capture detection in gas chromatography. J. Chromatogr., 98, 323-361.
- Penkett, S.A., Brice, K.A. (1986) The spring maximum in photo-oxidants in the Northern Hemisphere troposphere. Nature, 319, 655-657.
- Rosiek, J. , Sliwka, I. and Lasa, J. (1977) Destructive and non-destructive models of the coulometric electron-capture detector. J. Chromatogr., 137, 245-258.
- Schjoldager, J., Dreiem, R., Wathne, B.M., Johannesen, T., Stige, L., Tveita, B. (1984) Målinger av ozon, Østlandet - Telemark - Sørlandet, 1981-1983. Målinger av PAN, Telemark, 1983. Lillestrøm (NILU OR 34/84).
- Schjoldager, J., Dreiem, R., Krognes, T., Johannesen, T., Stige, L., Tveita, B. (1987) Målinger av ozon, Østlandet - Telemark - Sørlandet. Målinger av PAN, Telemark, 1984-1985. Lillestrøm (NILU OR 64/87).
- Shoemaker, G.R., Fenimore, D.C. and Zlatkis, A. (1965) Radiation Sources for Ionization Detectors in Gas Chromatography. J. Gas. Chrom., 3, 285-286.
- Singh, H.B., Hanst, P.L. (1981) Peroxyacetyl Nitrate (PAN) in the Unpolluted Atmosphere: an Important Reservoir for Nitrogen Oxides. Geophysical Research Letters, 8, 941-944.
- Stephens, E.R., Hanst, P.L., Doerr, R.C. and Scott, W.E. (1956) Reactions of nitrogen dioxide and organic compounds in air. Ind. Eng. Chem., 48, 1498-1504.

Stephens, E.R. (1969) The Formation, Reactions, and Properties of Peroxyacetyl Nitrates (PANs) in Photochemical Air Pollution. Advances in Environmental Sciences, edited by Pitts, J.H. and Metcalf, R.L. Wiley-Interscience, pp. 119-146.

Wentworth, W.E., Chen, E. and Lovelock, J.E. (1966) The pulse-sampling technique for the study of electron-attachment phenomena. J. Phys. Chem., 70, 445-458.

Zlatkis, A. and Fenimore, D.C. (1975) Recent improvements in electron capture gas chromatography. Reviews in Anal. Chem., 2, 317-342.

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

RAPPORTTYPE TEKNISK RAPPORT	RAPPORTNR. TR 5/91	ISBN-82-425-0258-7	
DATO JUNI 1991	ANSV. SIGN. <i>Storland</i>	ANT. SIDER 47	PRIS NOK 75,-
TITTEL PAN Measurement Technique, Part 1		PROSJEKTLEDER T. Krognæs	
		NILU PROSJEKT NR. O-91051	
FORFATTER(E) T. Krognæs		TILGJENGELIGHET * A	
		OPPDRAGSGIVERS REF.	
OPPDRAGSGIVER (NAVN OG ADRESSE) NILU			
STIKKORD PAN ECD Measurement			
REFERAT			

TITLE
ABSTRACT The technical details of the PAN measurement technique (calibration methods not included) used at NILU in the years 1986-1987 is described. A review of electron capture detector theory is included.

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