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meteorologyconsult inc., USA
INSTRUMENTS FOR ATMOSPHERIC RESEARCH • WWW.METCON-US-COM

AUTOMATIC ANALYZER FOR PAN AND PPN

AUTOMATIC PEROXYACETYL NITRATE (PAN) AND PPN GC-ANALYZER

Automatic gaschromatograph to measure PAN and PPN ind the atmosphere

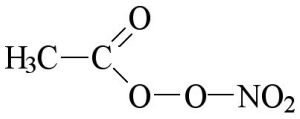
- Detection limit : ca. 50 ppt
- Detection limit with pre-concentration unit: ca. 5 ppt
- PC-controlled via USB-D/A oder PCMCIA-D/A
- Automatic peak integration, 6 measurements per hour standard
- Up to 10 measurements per hour as option
- PAN / PPN /MPAN version available
- PAN-calibration: Photolytic production of PAN and PPN from NO calibration gas

- Automatic GC-Analyzers for Methane and CO_2 for GAW-aplication.

- SF6-GCs also available

Metcon's PAN GC did successfully participate in the NCAR/NSF-funded intercomparison experiment PIE 2005 in Boulder, CO, USA. For results visit: HTTP://ACD.UCAR.EDU/~FFL/PIE_RESULTS.HTML

Peroxyaceticnitricanhydride (1), usually denoted by the trivial name peroxyacetylnitrate (PAN), and its homologeous such as peroxypropionicnitricanhydride (PPN, 2) and peroxymethacrylic nitric anhydride (MPAN, 3) play an important role in regional and global atmospheric chemistry.



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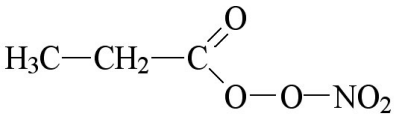

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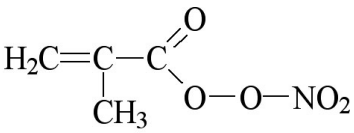

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PAN is the most abundant of these compounds with concentrations between a few ppt in marine background air to more than 10 ppb in urban air masses. It is formed photochemically from a wide variety of precursors, including ethane, butane, isoprene and acetone, in the presence of NOx. It is known as a strong lachrymator and for its phytotoxic properties. PAN also acts as an important reservoir for atmospheric odd nitrogen due to its stability at low temperature. It can therefore act as a transporting agent for reactive nitrogen like NO_2 into other regions of the atmosphere and can consequently have an impact on the production of tropospheric ozone.

PAN is a much better indicator of local photochemical production than ozone, which is transported downward from the free troposphere where concentrations of 50 to 100 ppb prevail due to transport from the stratosphere and from other continents. Last not least, the knowledge of PAN concentrations is important for the correct prediction of photochemical ozone production rates, as it has a large influence on the local concentrations of peroxy radicals.

PPN has been measured at mixing ratios between 4% and 20% of PAN. Its precursors (e.g. propane and 1-butene) are mainly of anthropogenic origin and PPN can therefore be used as an indicator of photochemical ozone formation involving anthropogenic hydrocarbons emissions. MPAN is produced simultaneously to ozone and PAN and it has only one precursor, isoprene, which is predominantly of biogenic origin. Simultaneous measurements of PAN, PPN and MPAN can provide information about the relative importance of biogenic and anthropogenic VOC emissions, a crucial step in the development of cost effective control strategies concerning the photochemical smog formation.

The Instrument

In 1992 the PAN GC-was developed, funded by the German EPA (UBA). Since that time the system has undergone a number of updates, the calibration procedure was tested indepth by research institutions. Instruments are operated successfully in many countries worldwide.

The automatic PAN/PPN-Analyzer is suited for 19″-rackmounting and combines a PC-controlled, fully automated analytical instrument with a reliable and easy to handle calibration method. The limit of detection for PAN is < 50 ppt (< 30ppt under optimum conditions) and the linear dynamic range extends to 10 ppb or more. The optional thermoelectric Preconcentration Unit provides a detection limit to < 5ppt at the same sample rate (12/h) and without the need for liquid nitrogen or dry ice. The dynamic Calibration Unit is based on the photochemical synthesis of PAN or PPN from an NO calibration gas in a flow system.

The PAN/PPN-Analyzer comprises gas chromatographic separation on capillary columns at sub-ambient temperature with electron capture detection. The columns are mounted in a compact temperature controlled oven, cooled by Peltier elements. Temperature fluctuations are less than 1 K??. A dual thermo-stat permits the operation of the GC over a wide range of ambient temperatures (5-30°C). Purified and pre-conditioned nitrogen is used as the carrier and make-up gas. Back flushing of the pre-column prevents contamination and reduces analysis time by preventing substances with long retention times from entering the main column and the detector. Sampling, injection and column switching is accomplished with a pneumatically actuated 10 port valve (VALCO). A by-pass arrangement for the sample flow provides short residence times in the sample line.

A hybrid system containing both oven modules and thus combining the advantage of a faster PPN (and MPAN) analysis with the use of CCl_4 as internal standard can be provided upon special request.

PAN-GC (upper instrument) and calibration unit below

Automatic Operation

A new PC-Software (WIN XP) was designed that facilitates the control of the GC-system, as well as data-acquisition and reduction. A number of different I/O-boards (USB - DA or PCMCIA/PC-Card) manufactured by Measurement Computing Inc., USA are implemented in the software. The following modules are part of the software package. (WIN XP):

- Control of the GC and its continuous operation, collection of control parameters for remote operation
- Data acquisition of the ECD-signal and automatic integration of the peak area.
- Control of the calibration device and automatic initiation of the calibration procedure, provision of control parameters
- Module to view the raw data and to re-integrate peaks, if necessary
- Module to evaluate time-series of the integrated peaks, e.g. CCl_4, PAN, PPN.

Peak finding occurs automatically after the approximate position and width of the peaks have once been marked in a test chromatogram on the PC-screen. During the subsequent automatic operation of the GC, the exact peak position is automatically optimized and integration occurs automatically by a least squares fitting. Peak areas are stored along with the concentrations derived from calibration factors. The flows of the sample air and the slope of the baseline (as an indicator of the performance of the ECD) are also stored and are used to derive quality-flags that can be transmitted to a remote computer.

Calibration Unit

The calibration unit produces a continuous, stable flow of known PAN or PPN concentrations in air. It is based on the photochemical synthesis of PAN or PPN from an NO-calibration gases (ppm range) in a flow reactor with subsequent dynamic dilution to concentrations of 0.1 to 30 ppb in an air flow of 1-10 l/min. NO is used instead of NO_2, because of the better stability of NO calibration gases. Purified ambient air is used for dilution purposes in order to save expensive zero air. The procedure is semi-automatic. The PAN-Calibration Unit is connected to the PAN-GC via a pneumatic PFA-valve. In the calibration mode samples are drawn from the overflow assembly of the calibration unit. The required peroxyacyl radicals are produced by photolysis of acetone or propanal. The peroxy radicals obtained from the photolysis first oxidize the NO to NO_2, which then forms the PAN (or PPN). The PAN concentration is obtained from the NO-mixing ratio in the NO-standard (μ_{NO}), the flow of the standard (Φ_{NO}), the total flow after dilution (Φ_{total}), and the reaction yield for PAN (Y_{PAN}).

$$\mu_{PAN} = \mu_{NO} * Y_{PAN} * (\Phi_{NO}/\Phi_{total})$$

The Calibration Unit was thoroughly evaluated during the QA-program of the German Tropospheric Research Focus using two independent techniques. The PAN yield was determined to be 92 % +/- 3 %. It was found to be stable over a wide range of operating conditions, i.e. 0.1 -30 ppb PAN in 10 l/min. A comparison of several calibration units yielded < 10% disagreement, including possible errors in the calibration gases used by the different investigators. The yield for PPN is similar or slightly higher than for PAN.

Pre-concentration Unit

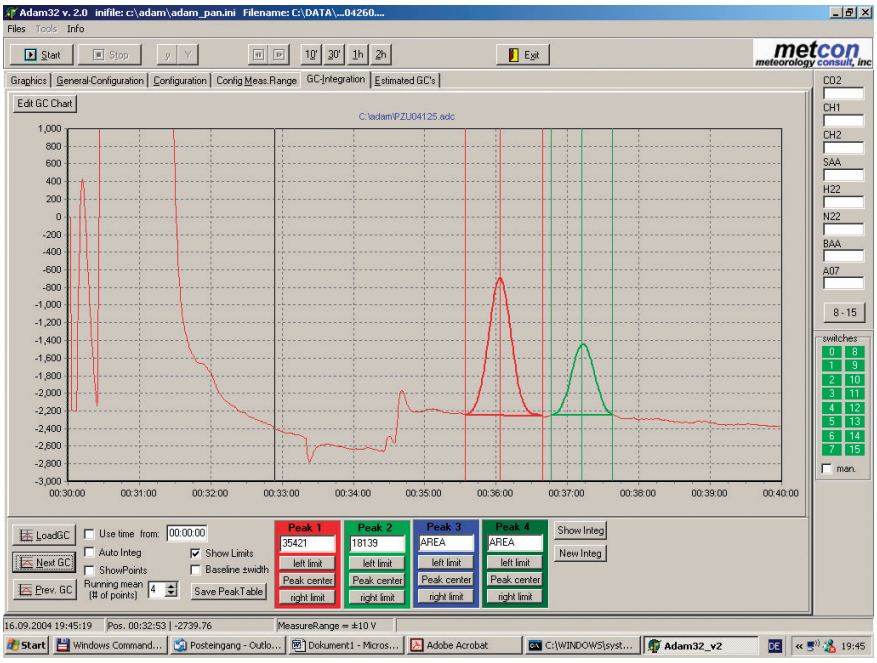
The pre-concentration unit employs enrichment of PAN based upon Henry's law in a Peltier-cooled device at constant temperature. Sample injection is achieved by flash heating. The unit is contained in a 3HU 19" housing, which mounts directly under the GC, and is connected to the 10-port valve instead of the standard sample loop. The unit requires only electrical power. Sample injection is actuated via the PC and the relay board of the GC. The detection limit for PAN is approx. 5ppt. The measurement frequency remains unchanged at up to 12 chromatograms per hour.

NEW PAN GAS-CHROMATOGRAPHY

NEW PAN GAS-CHROMATOGRAPHY

A column combination is available, which allows the simultaneous measurement of PAN ($CH_3C(O)OONO_2$), PPN (peroxypropionic nitric anhydride, $C_2H_5C(O)OONO_2$), and MPAN (peroxymethacrylic nitric anhydride, $C4H_5C(O)OONO_2$).

The higher homologues are formed in the atmosphere just as PAN from the respective organic precursors and NO_2. Of particular interest is MPAN which is formed during the photochemical degradation of isoprene in the presence of NOx. American measurements (Williams et al., 1997) demonstrated that the simultaneous measurement of ozone, PAN, PPN and MPAN provides valuable information on the biogenic or anthropogenic origin of ozone. Such information is, e.g., important for decisions about NOx vs. VOC reduction strategies for smog abatement. (Williams, J. et al., Regional ozone from biogenic hydrocarbons deduced from airborne measurements of PAN, PPN, and MPAN, Geophys. Res. Let., 24, 1099-1102, 1997)



Example of a Chromatogram: First peak is CCl_4 (red), second peak is PAN (green). The graph represents a measurement in April at a remote mountain station in Germany.

THREE VERSIONS OF THE PAN GC:

1. The standard version allows the measurement of PAN, CCl_4 and CH_3CCl3. Analysis time is about 6-10 min. Since the atmospheric concentration of CCl_4 is rather constant, the CCl_4 peak can be used as an internal standard for establishing the response of the ECD in between calibrations.
2. The new version has a column oven module that allows the separation of PAN and PPN. Analysis time is about 5-6 min. The analysis of MPAN should also be possible with this column (currently being tested).Calibration should be done more frequently (daily) since CCl_4 is no longer available as internal standard. (Please see improvement of PAN-calibration below).
3. Upon request, a version that contains both oven modules can be provided. The advantage of this (more complicated and more expensive) version is that CCl_4 can still be utilized as an inter-nal standard.

ZERO AIR FOR DILUTION:

A zero air module is available that produces PAN free air at flow rates of up to 8 l/min STP from ambient air. The new module eliminates the need for compressed air from cylinders for dilution of the PAN mixture and allows PAN calibration to be conducted more frequently and routinely at reasonable cost. The calibration device can be fully controlled by the software which is supplied with the gaschromatograph. TTL-compatible relays, allow the actuation of the all relevant functions. The flows of the dilution air and the primary NO-premixture can be measured as analog signals and stored to disk. Using a remote access software like PCAnywhere or Ultra-VNC all functions are accessible by a remote Computer.Besides PAN PPN can be calibrated with the same device as well.

EXTENT OF DELIVERY (depending on individual setup)

PAN-GC

- 19″ 3HU gas chromatograph, including an ECD Detector and ECD-Electronics.
- cartridge for carrier gas conditioning
- tubing for connection to gas tanks and pump
- PCMCIA-ADC/IO-board (for Notebooks) or USB D/A.
- data acquisition, integration and control software

PAN-CALIBRATION

- 19″ 2HU photochemical PAN generator
- supply tubing

INSTALLATION, SET UP

- delivery includes a1 _day installation and training. Travel expenses will be charged separately.

SUPPLEMENTARY EQUIPMENT TO BE PROVIDED BY THE CUSTOMER:

- nitrogen (purity > 99.999 %), cylinder pressure regulator, cleaned and specified for ECD use
- zero air (free of NOx), and cylinder pressure regulator, brass, 1 stage
- dilution air ca. 5 l/min, PAN-free
- NO-in-N2-calibration gas (ca. 10 ppm)

SPECIAL REQUIREMENTS FOR OPERATION OF THE ECD

Designated as the detection unit is a modular system of Therm isher. Operation of ECDs is subject to specific administrative regulations. A copy of the official operating permit for the measurement site must be received by the supplier prior to delivery of the ECD-module.

SPECIFICATIONS PAM-ANALYZER

METHOD	Gas chromatography with electron capture detection
PRE- AND MAIN COLUMN	Wide bore capillary columns
DETECTOR	Prepared for installation of a Therm Fisher ECD
OVEN	Peltier-cooled and temperature controlled by Pt100;
SAMPLE INJECTION/COLUMN SWITCHING	Pneumatically actuated VALCO 10 port valve with external sample loop
CARRIER GAS/MAKE UP GAS	Nitrogen 99.999%, total flow < 50 ml / min
PURIFICATION	Cartridge for carrier gas conditioning and purification
DETECTION LIMIT	< 50 ppt (< 30ppt under optimum conditions)
MEASURING FREQUENCY	12 measurements per hour
CALIBRATION	Approximately once a week (see below)
OPERATION TEMPERATURE	5 - 30 °C
CONTROL / DATA ACQUISITION	USB-Data-Acquisition device to any PC
SOFTWARE	Windows XP program for data acquisition, peak-integration and control
DATA FORMAT	ASCII files for PAN concentrations and for the raw data
ELECTRICAL POWER	230/110 VAC; 200 W (without pump)
DIMENSIONS	3 HE 19″-rack housing (45x45x13.5 cm)
WEIGHT	Approx. 15 kg

PRECONCENTRATION-UNIT

METHOD	Peltier-cooled pre-concentration loop with flash heating
DETECTION LIMIT	Approx. 5 ppt for PAN
MEASURING FREQUENCY	12 measurements per hour
ELECTRICAL POWER	230/110 VAC; 200 W
DIMENSIONS	3 HE 19″-rack housing (45x45x13.5 cm)
WEIGHT	Approx. 7 kg

CALIBRATION-UNIT

METHOD	Continuous photochemical synthesis from an NO calibration gas; conversion efficiency 90% +/-5%
GASES AND CHEMICALS	NO in nitrogen: e.g., 10 ppm (approx. 1 ml / min); zero air (< 50 ml / min); acetone (p.a.)
DILUTION GAS	Membrane pump with purification cartridge
MAX. AMBIENT TEMPERATURE	30 °C (higher temperatures optional)
ELECTRICAL POWER	230 V/110V; 100 W (without pump)
DIMENSIONS	2 HE 19″-rack housing (45x45x9 cm)
WEIGHT	Approx. 12 kg

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