Eraly
& Associés
The Elemental Analysis

NITROGEN Analyzer by Chemiluminescence

Standards **AST D4629 / ASTM D6069 / ASTM D 5176 / ASTM D 5762 /**
NF EN 12260 / NF M 07-058 – Licence TOTAL

LUMAZOTE

TECHNICAL BROCHURE

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1 Summary

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The Elemental Analysis

The CENTRE DE RECHERCHES TOTAL (Research Center of TOTAL) developed this apparatus to answer a major problem of oil industry:

To measure automatically and rapidly the very low contents of nitrogen in petroleum products (to 20 ppb) in routine analysis,

And in the best conditions possible regarding:

- Accuracy.
- Rapidity.
- Implementation.
- Comfort of using.

LUMAZOTE is the result of this research, and appears to answer to these requirements.

In some particular conditions of using, obtained performances may be notably better than those given.

1) RESUMED GENERAL CHARACTERISTICS

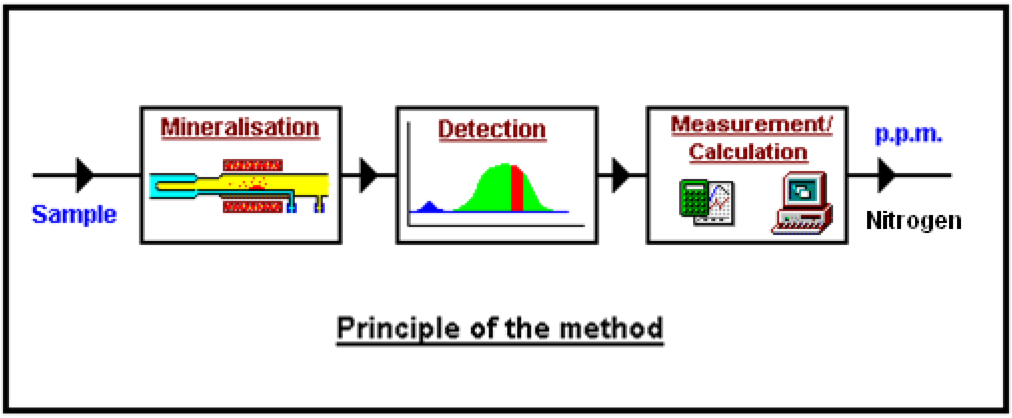
1.1) *Range of application*

Its overriding range of application concerns the **liquid petroleum products (NF M07058 and ASTMD 4629)**. It can be enlarged to all organic substances compatible with the method requirements.

- Solvents.
- Oils.
- Synthesis products.
- ...

1.2) *Principle of the method*

The analysis goes on in three phases:



- Destruction of the sample by pyrolysis → *Mineralisation system*
  and oxidation of the obtained gases **N → NO**
- Detection of **NO** formed. → *Chemiluminescent detector*
- Measurement, signal treatment, calculation. → *Integrator and calculator*

1.3) *Detection of NO by Chemiluminescence*

Luminescence is the capacity of lot of substances to emit light when excited. This phenomenon (produces with good energy efficiency) is called chemiluminescence when it is provoked by a chemical reaction.

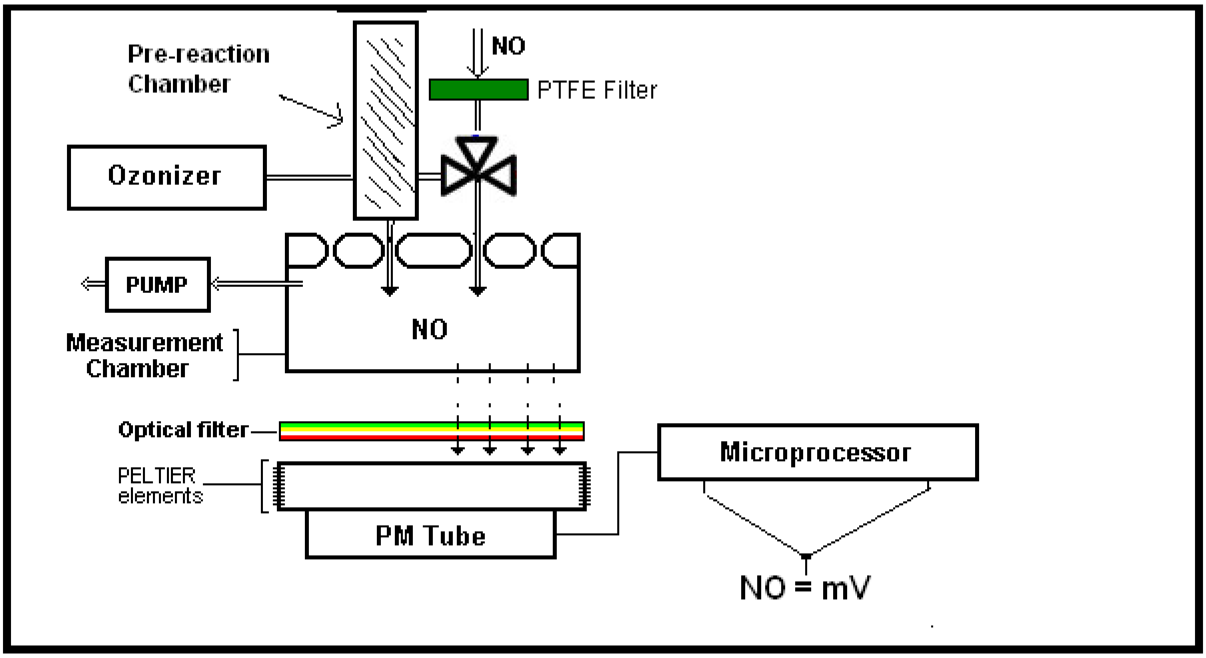
In our precise case, the principle is to detect photons emitted during reaction between nitrogen monoxide NO and ozone O_3.

$NO + O_3$. → NO_2*+ O_2
NO_2* → NO_2 + hv (photon)

* excited form

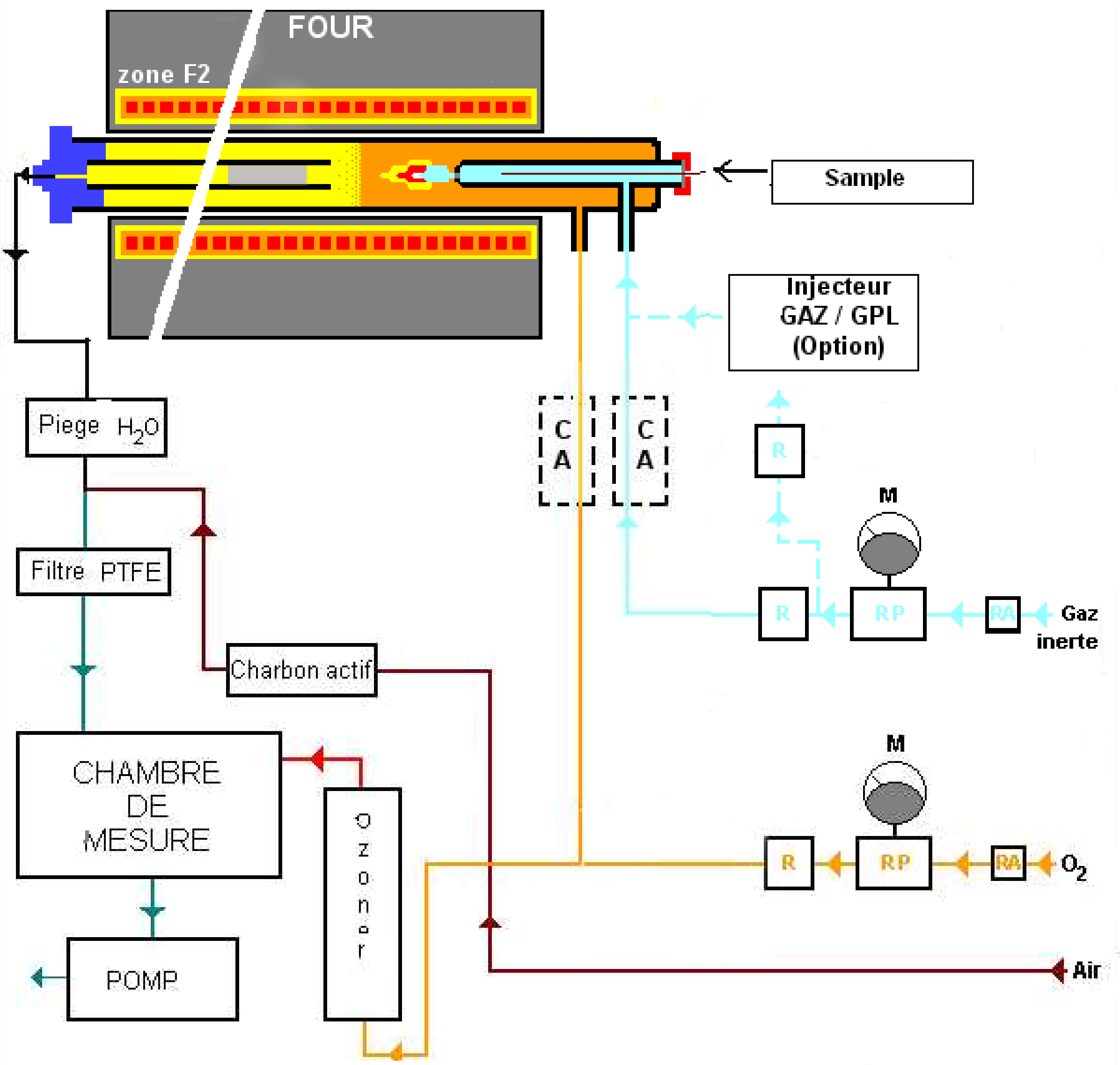
The quantity of light with determined wavelength, filtered (in order to eliminate interference with other substances which also generates chemiluminescent phenomenon) and measured by a photomultiplier tube.

The signal detected and amplified gives the instantaneous NO concentration.



1.4) *Gas flow sheet*

Gas flow sheet



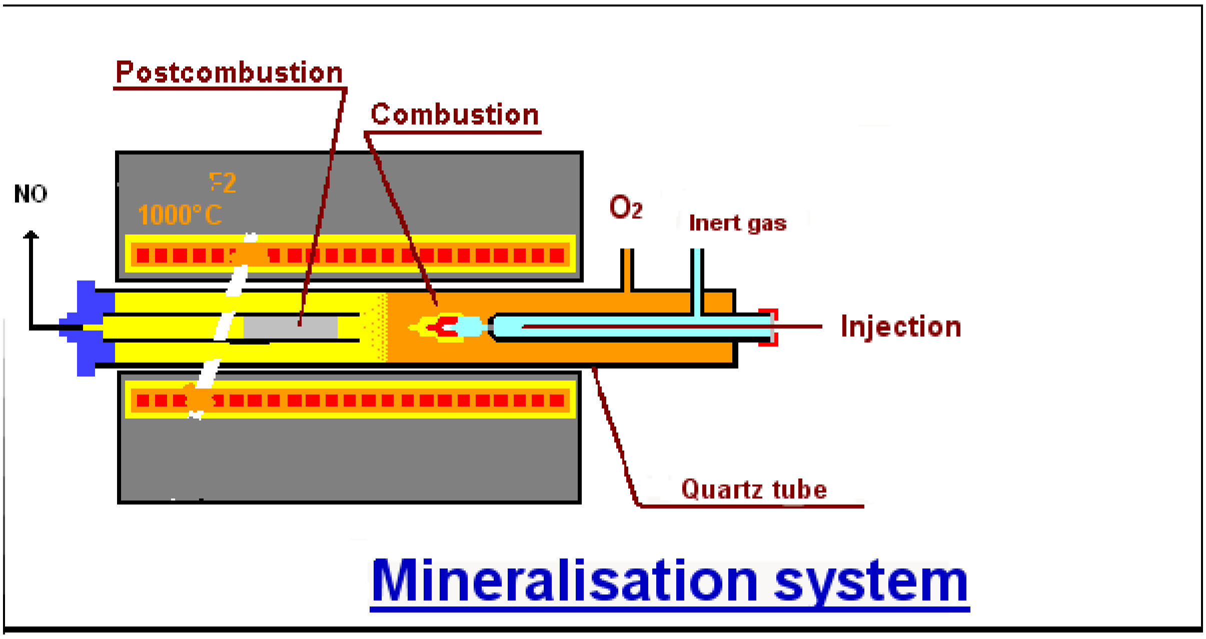
RA : Gas admission valve
R : Flow control valve
Zone F1 : 700°C

RP : Pressure regulator
CA : Activated carbon filter (option)
Zone F2 : 1000°C

1.5) *Mineralization system*

It is composed with a quartz tube which contains another small quartz tube filled by copper oxide, and one furnace F2:

F2 furnace under oxygen at 1050°C for oxidation of the sample.

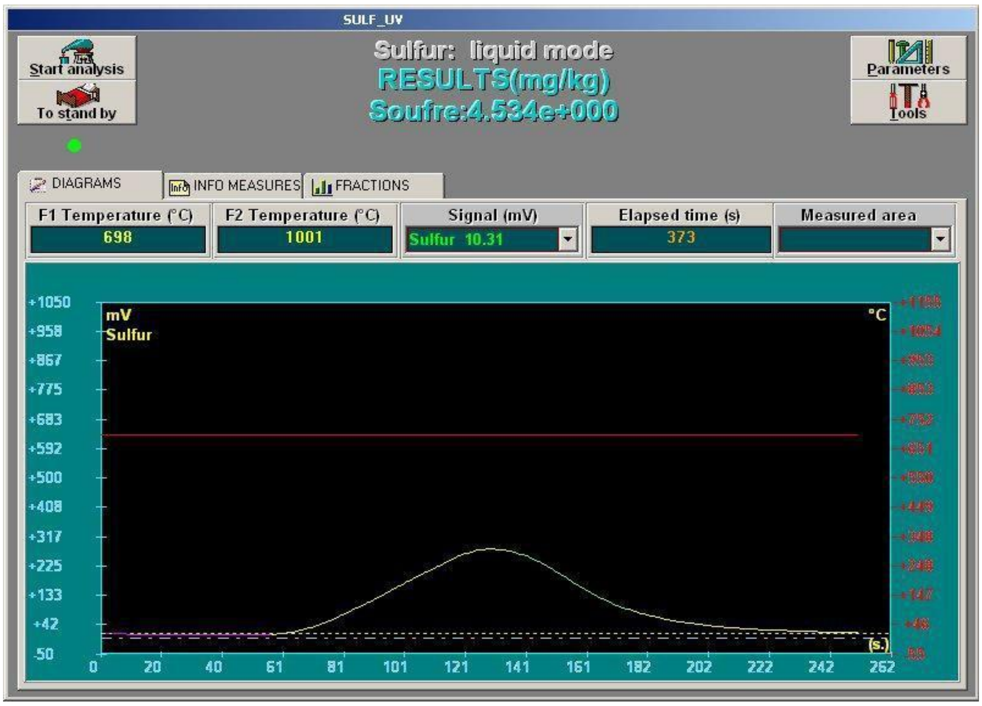


1.6) *Integrator and calculator*

NO carried in the measurement chamber of the detector provokes the apparition of a **NO** “peak” whose surface is proportional to the content of Nitrogen in the sample.
An electronic integrator of high precision, associated with a computer, insures the control of the analysis and the calculations to express the results.
The computer permits the keyboarding of the sample characteristics (volume, density, weight, reference …). It reads the integrator value, calculates the result and displays it in real time, as well as the concentration graph according to time.
Depending on the type of trial requested, the result can be a calibration coefficient, a “blank” value, a drift measurement or an analysis.
At the end of trial, the result and all the analysis parameters are saved on hard disk, and an analysis bulletin is printed.

The computer also manages:

- The syringe pusher process.
- Some alarms.
- The saving of the results, measurement parameters, preferences, and so on.
- Maintenance tools.
- Three levels of protection by passwords.
- The possibilities to exploit the results file with a spreadsheet.
- And so on...



Sulfur: liquid mode
RESULTS(mg/kg)
Soufre:4.534e+000

F1 Temperature (°C): 698
F2 Temperature (°C): 1001
Signal (mV): Sulfur 10.31
Elapsed time (s): 373
Measured area:

2) CALIBRATION AND MEASURE

The proposed method is a comparative method. So it is necessary to make a preliminary calibration.

This calibration has to be made with a known product, and considered as a reliable “standard” or “reference”.

The precision of the results is directly linked to the precision of the calibration products.

Standards and customs recommend choosing calibration products as close as possible of the products to analyze, regarding content and nature.

The apparatus calculates automatically the mean value of calibrations, as well as repeatability from 5 trials.

The validation criterions of good working are the following ones:

In liquid mode / calibration:

- Stable calibration coefficient at long term (±5 % of initial calibration values), own for each apparatus (generally near of 1e-008 in range 1) and proportional for the other ranges.
- Repeatability near of the following values, depending on contents :
- ± 10 % for 0.05 ppm level
- ± 5% for 0.1ppm level
- ± 1 % for 5 ppm level
- ± 1 to 2 % for more than 20ppm level

The calibration must be made for each analysis mode and each range. It is recommended to verify it daily, depending on the results precision to be reached.
The experience will show that the middle term drifts are very low and that there is a good coherence of coefficients ratios between ranges and modes.
Knowing the experimental approximations, it is always possible (for a range and / or a mode) to force an arbitrary coefficient calculated from a calibration made on another range.

2.1) *Choice of calibration mode*

Response of the detector is linear for each selected range or measure scale. So, calibration on one point is enough.

However, MIPO 5 software offers possibility to make multipoint calibration for determination of calibration curve.
This calibration mode is significant only if made on at least 3 points (down, middle and up of range).
Generally, it confirms the effective linearity of detector response, and the passage to zero (or very near).

Note: the announced characteristics are verified and apply to current petroleum products at the condition the analysis are normally conducted, in cleanness conditions and with the recommended adjustments.

It is possible to gain more sensitivity when working the nearest possible of the inferior limit, with more precautions than standard conditions:

- Careful supervision of the cleanness of the tube, connectors and gases circuit.
- Preliminary trials to determine the optimum conditions of mineralization.
- Establish the coefficient on a 5 trials mean.
- Make 2 trials (or more) per determination.

2.2) *Choice of the analysis mode*

Liquid mode is used for products which can be sampled and injected directly with a micro syringe (50µl).
The sampling volume is measured on the syringe scale (known in lump with the density of product).

Gas mode is used for gaseous products, with a gas syringe (5 to 25 ml), sampling volume measured on the syringe scale. Its implementation is the same than with liquid mode.

Remark : A solid product can also be diluted for analysis in liquid mode.

The user can chose the analysis mode depending on the means of its laboratory and on the researched results.

2.3) *Choice of the measurement ranges*

To be realized on the detector depending on the Nitrogen contents to reach.

- **liquid mode (50 µl syringe)**

Recommended ranges, with large possible covering:

- range 0,5 : < 1 ppm
- range 1 : 0.5 to 10 ppm
- range 10 : 5 to 100 ppm
- range 50 : > 50 ppm

2.4) *Parameters choice*

The apparatus is delivered with stored parameters automatically called by default.
Without other appreciative elements, we recommend to use these parameters by default, or to research and call the parameters of a previous comparable trial in the stored trials file.

It is interesting for certain products to optimize the analysis parameters in order to:

- reduce the analysis duration
- increase eventually the sensitivity and the repeatability of responses
- facilitate and secure a using procedure

These new chosen parameters can be stored as the new parameters by default.

3) INSTRUCTIONS OF INSTALLATION

3.1) Mechanic

The apparatus must be set on a laboratory bench top able to receive it in good conditions of safety and access:
Support the weight of the analyzer (≈ 35 kg) and associated computer and printer (≈ 15 kg) make the following spaces:

- length :

Apparatus (≈ 81 cm) + 60 cm space on left side (UV detector rack for maintenance) associated informatics: about 500 to 600 mm for computer + about 500 mm for printer. Total length: about 2.8 m

- depth :

Apparatus ≈ 55 cm + back space for ventilation (≈ 10 cm) Total
depth about 65 cm

- height :

Apparatus ≈ 48 cm (31 + 17) - As the furnaces are placed on the top of the analyzer, it is preferable to allow the above space free (if not, allow at least 50 cm)

3.2) Electric

The apparatus has to be connected to the 220 V ∿network – 50 Hz – single phased, with a 2 poles tap + ground 10/16 A.

- Consumption of energy on Analysis mode ≈ 1100 W (about 600 when stand by)
- The quality of the network must be compatible with a good working of informatics systems.

3.3) Gas

The apparatus needs 2 gas supplies:

- Oxygen (N48 quality – purity 99.998 %)
- Inert gas (Argon recommended) (N55 quality – purity 99.9995 %)

Supply pressures must be comprised between 2 bars minimum and 3 bars maximum.
Consumption in analysis mode about 12 l/h (no consumption when awake)

Fittings on the apparatus are insured by 2 double ring connectors (type Swagelok) for external ∅ 1/8” (3.17 mm) tube. About 2 m of tube are provided with the apparatus. (fittings can be rigid: copper or stainless steel tube in same dimensions).

Even if purity of gases is normally guaranteed, it is also essential to verify that lines which carry gases to the analyzer are perfectly clean and tight.

3.4) *Nature of inert gas*

- We **recommend using Argon**.
- Helium can be used as inert gas (same purity).

However, its viscosity being different, it is necessary to make corresponding corrections on marks of flowmeters balls.

- Do not use NITROGEN.

3.5) *Environment*

We recommend to stabilize the working ambient temperature between 15 and 25°C – in any case, never more than 30°C (if risks of working in 25 / 30°C conditions, inform us for implementation of eventual particular disposal).

Avoid exposing the analyzer in a too hot or too cold place (e.g.: sun behind a window or ventilation of an air conditioner).

3.6) *The computer*

The software insuring the management of **SULF UV SL** and its options works under *Windows XP* environment.

Minimal configuration required:

PC compatible Windows XP, Vista, Windows 7....
Processor 1GHz (or more)
RAM Memory: 512 Mo. (or more)
Hard disk: 10 Go. (or more)
Available serial port (COM1 à COM4) allowing a transfer speed of 28800 bauds.
Screen SVGA (800 x 600).
Colour printer.

4) FRONT FACE OF ANALYSER

(1) Front face –detector

(1-1) detector keyboard
(1-2) detector indicator
(2-2) Interfaces rack (access reserved to or allowed ERALY maintenance)

(6) Syringe pusher

(6-1) syringe support

(8) Combustion tube

(8-2) Output joining piece

(8-4) Teflon tube 1/8” PFA for joining tube □detector

(10) Furnace

FRONT FACE OF ANALYSER