TECHNICAL NOTE

ThermoFinnigan

TSN 254/EA
Date: December, 2002

From: Nicola Longo

To:	**SERVICE OPERATIONS AND ALL DISTRIBUTORS**	**Product Line**
	TECHNICAL SUPPORT DEPARTMENT	☐ GC
		☑ **EA**
Re:	**ANALYTICAL TROUBLESHOOTING**	☐ MSTR
Instr:	**FLASHEA 1112**	☐ ....

Issue	Category	Implementation	Level
☐ Hardware	☐ Mandatory	☐ Priority	☑ **On Site**
☐ Software/Firmware	☐ Safety Improvement	☐ On first field visit	☑ **In your Laboratory**
☑ **Operative Procedure**	☑ **Reliability Improvement**	☑ **Only if the problem occurs**	☐ High Complexity
☐ Maint Procedure	☑ **General Info**	☐ Not required	☑ **Medium Complexity**
☑ **Documentation**	☐ No Parts Required	☑ **During the installation**	☐ Low Complexity
☐ Spare Parts	☐ Free Of Charge	☐ On request	☐ ....

Please find enclosed the *Analytical Troubleshooting* for all FlashEA 1112 analyzers.

This important tool has been prepared to help you in addressing "analytical troubles" through all analytical expertise currently available in the factory.

The Analytical Troubleshooting is also available on the web site.

Please distribute this document to relevant people in your service organization.

Thermo Finnigan

FlashEA 1112 – Analytical Troubleshooting

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FlashEA 1112 – Analytical Troubleshooting

This chapter provides information to help diagnostics of instrument troubles and a guide to solve them. The following Tables include a summary of the main problems. Also there are specific descriptions of several troubles with typical chromatograms to help you during the troubleshooting procedure.

TABLE 1 – List of analytical troubleshooting

Problem	Diagnosis	Remedy
High N blank	Presence of leak.	Check that Helium and Oxygen lines are leak free if not eliminate possible leaks.
	Oxygen line or cylinder contaminated.	Purge the line, or replace the cylinder.
	Autosampler not purged *(see page 4)*	Check that the flow is correct (100 ml/min for 1 drum, 150-200 ml/min for more drums)
High constant N blank in several sequential runs	Oxygen cylinder contaminated.	Replace the Oxygen cylinder.
	Presence of leak in the autosampler.	Identify leaks and remove them.
Decreasing N blank values.	Oxygen line contaminated.	Purge the line 10-20 minutes. Repeat blank run.
Increasing N blank value.	Copper exhausted *(see page 13)*	Replace the reactor.
Tailing on N peak	Bad combustion.*(see page 5, 10)*	Decrease weight of sample, increase oxygen quantity, clean ashes.
High C blank.	Tin capsules contaminated.	Check capsule box, tweezers, work bench must be clean.
	Memory effect to bad combustion.	Remove ashes and/or analyze lower amount of sample.
Tailing or split on C peak.	Too many ashes.	Check ashes and remove them.
	Bad combustion *(see page 5)*	Decrease weight of sample, increase oxygen quantity.
	MAS200 cover position not correct. *(see page 5)*	Check the MAS200 cover position.
Bad separation between N and C.	High Nitrogen blank value.	Check the Nitrogen blank. Repeat the analysis.
	Copper exhausted *(see page 13)*	Replace the reactor.
Peak between N and C.	Oxygen line contaminated	Exclude autosampler and check the oxygen blank.
	Inadequate Oxygen purity.	Exclude autosampler and check the oxygen blank.
	Purge of MAS200 with multi-drums incomplete *(see page 4).*	Increase the Helium Reference flow to 150-200 ml/min.
	Sample delay not correct *(see page 9)*	Increase or decrease the sample delay time.
Negative peak between N and C	Helium and Oxygen pressure are not the same in CHN/O and CHNS/O configurations *(see page 3)*	Regulate both pressures to the same value 250 kPa.
Split on H peak.	The tube connecting reactor and GC column is clogged.	Cut off the clogged tube portion.
Retention time very delated respect to the typical chromatogram.	Presence of leaks or obstructions in the pneumatic circuit.	Perform a leak test or reach and remove the obstruction.
	Anhydrone exhausted *(see page 14)*	Change Anhydrone.

TABLE 2 – Analytical Troubleshooting related to sample nature.

Problem	Diagnosis	Remedy
Sulfur peak: **tailing or split** *(see page 15)*	Incomplete Sulphur conversion (for example in soil, leaves, plants, samples with inorganic sulphur).	Add about 10 mg of vanadium pentoxide to the tin container before weighing the sample and mix them.
Hydrogen peak: Split (sometimes also ghost peak on Carbon peak) *(see page 16)*	Presence of fluorine in the sample	For CHNS/NCS use Silver capsule (P/N 240.054.05) and weigh 0.2-0.4 mg of sample). For CHN fll the reactor with a specific absorber mix before the catalyst.

# Effect of the Helium and Oxygen pressure on the analysis.

The nominal pressure of gas supplies for all configurations of the FlashEA1112 elemental analyser should be: 250 kPa for Helium and 250 or 300 kPa for Oxygen according to the analytical configuration.

For CHNS/O and CHN/O with two furnaces it must be 250 kPa, for all other configurations must be 300 kPa.

Trouble: if the Helium and Oxygen pressure are not the same (250 kPa) in CHNS/O and CHN/O configurations with two furnaces, there is a negative peak between Nitrogen and Carbon peaks.

Solution: It is necessary to regulate both pressures to the same value to eliminate the negative peak and to have a good separation between Nitrogen and Carbon peaks.

Typical CHN chromatogram
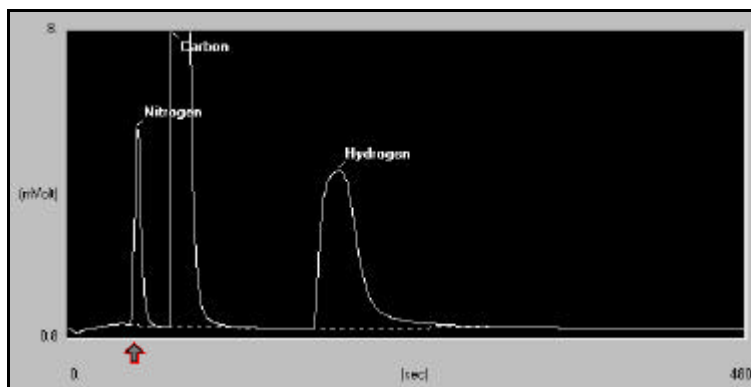
CHN chromatogram with an Oxygen pressure higher than Helium pressure
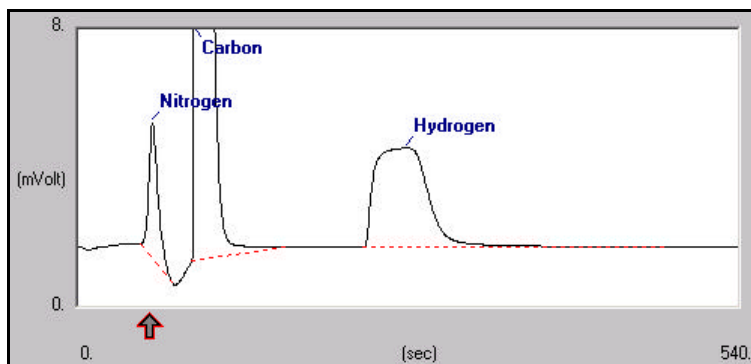
MAS 200 Autosampler: Influence of Helium flow reference line and cover position.

1) Influence of Helium flow reference line:

The purpose of the Helium Reference line is to degas the area where the samples are housed in the autosampler.

The nominal flow used for all configurations of the FlashEA1112 elemental analyser should be 100 ml/min if the autosampler is provided with the first 32-position sample tray.

Trouble: In the chromatogram there is a peak between Nitrogen and Carbon when the MAS 200 is provided with more sample trays because the purge is not complete.

Solution: Increase the Helium flow from the reference line to 150-200 ml/min.

Effect on CHNS chromatogram
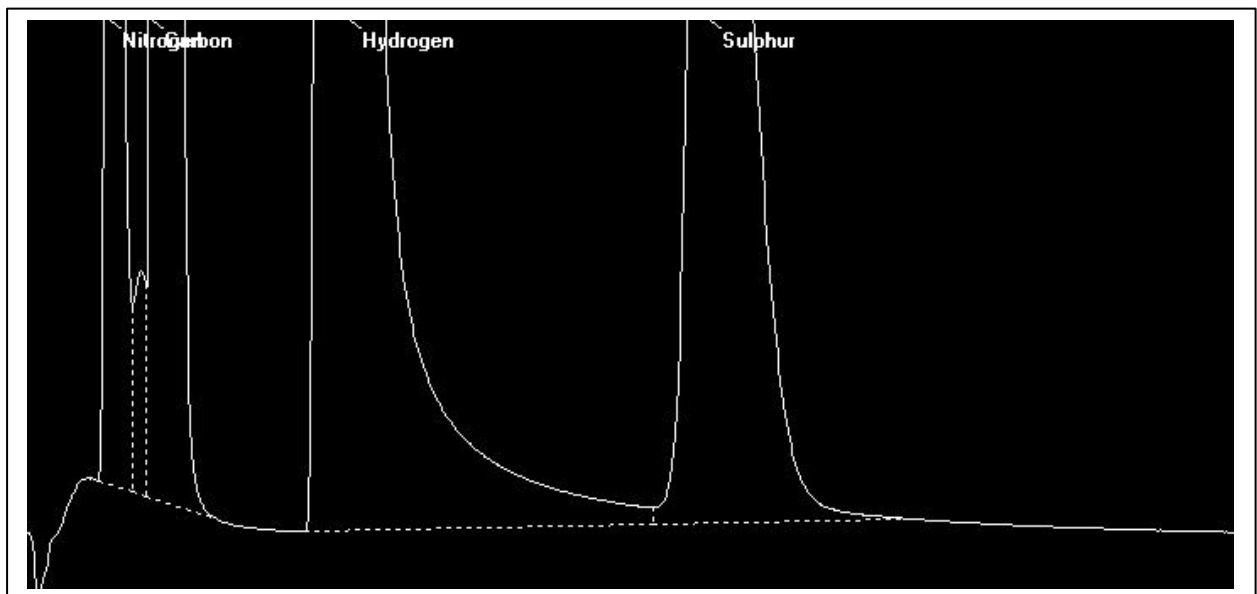
2) Effect of the MAS 200 cover position

The autosampler has a protection cover that is positioned over the sample tray. A complete deareation of the area where samples are housed is only possible if the cover is placed in the correct way.
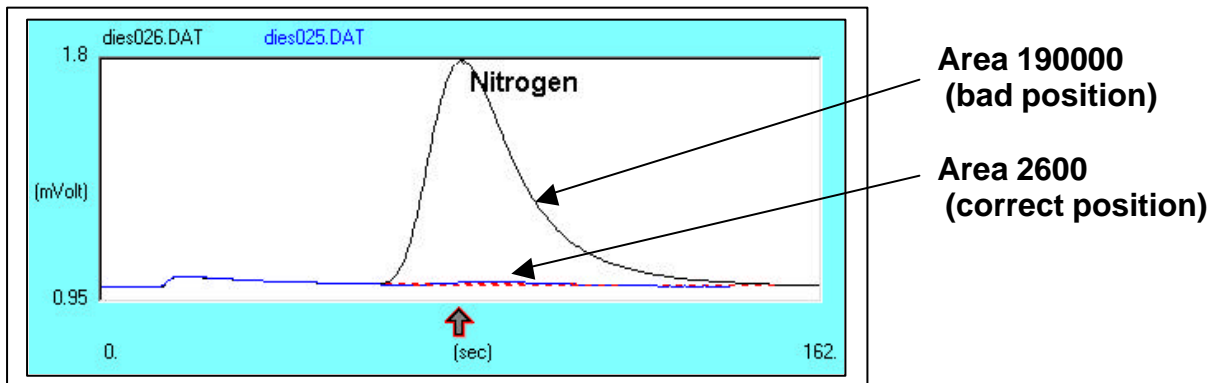
Trouble: Bad separation between Nitrogen and Carbon, high Nitrogen blank value.

Solution: Put the cover in the correct position.

CHNS chromatogram where the cover is positioned in an incorrect way.
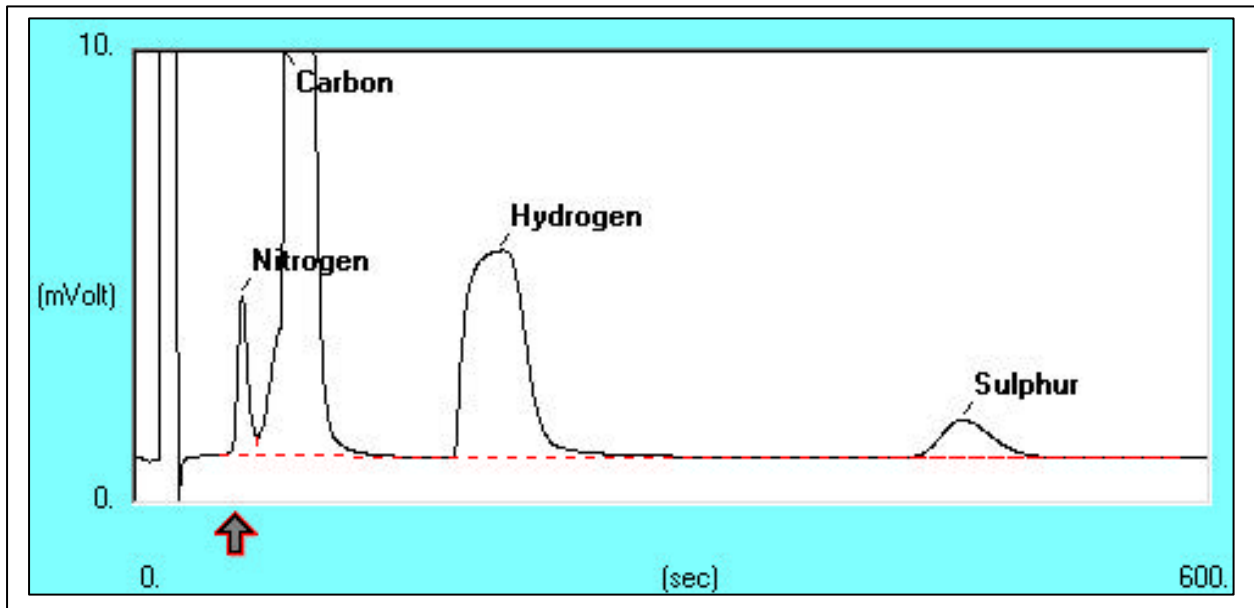
Blank analysis in Nitrogen/Protein configuration

Area 190000
(bad position)

Area 2600
(correct position)

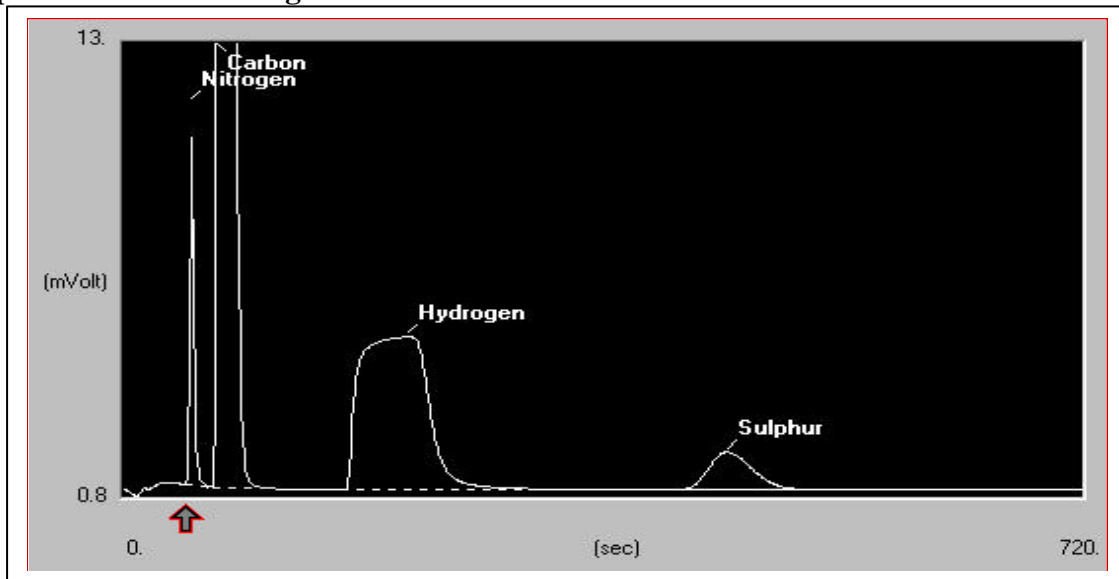# Bad combustion in CHN, CHNS and NCS configurations:

Bad combustion of sample due to: high weight of sample, required oxygen not sufficient, too many ashes catalyst exhausted.
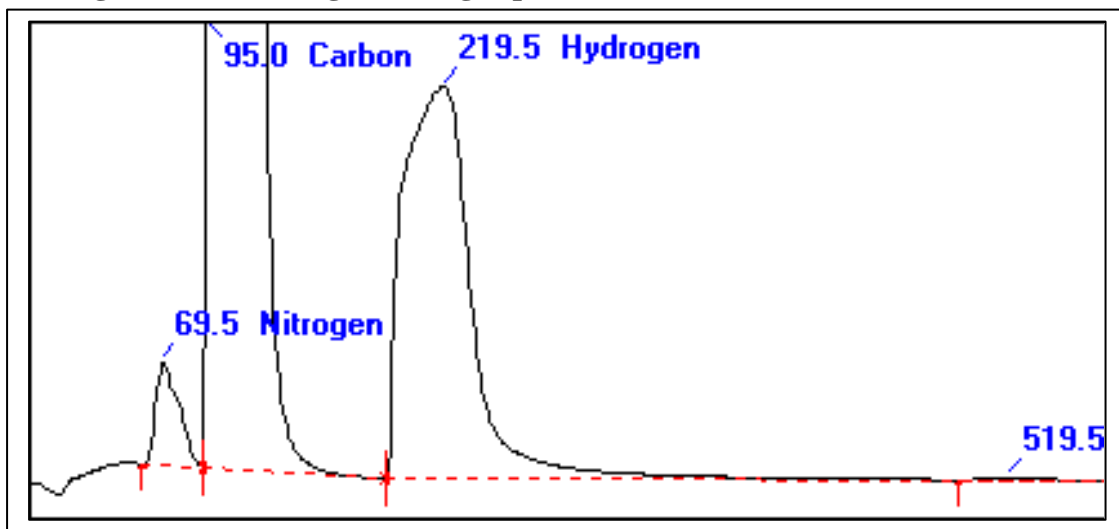
Trouble: Tailing on Nitrogen peak
Bad separation between Nitrogen and Carbon peaks
Split or tailing on C peak

Solution: Decrease the weight of sample, increase the oxygen quantity, clean the ashes, change the catalyst.
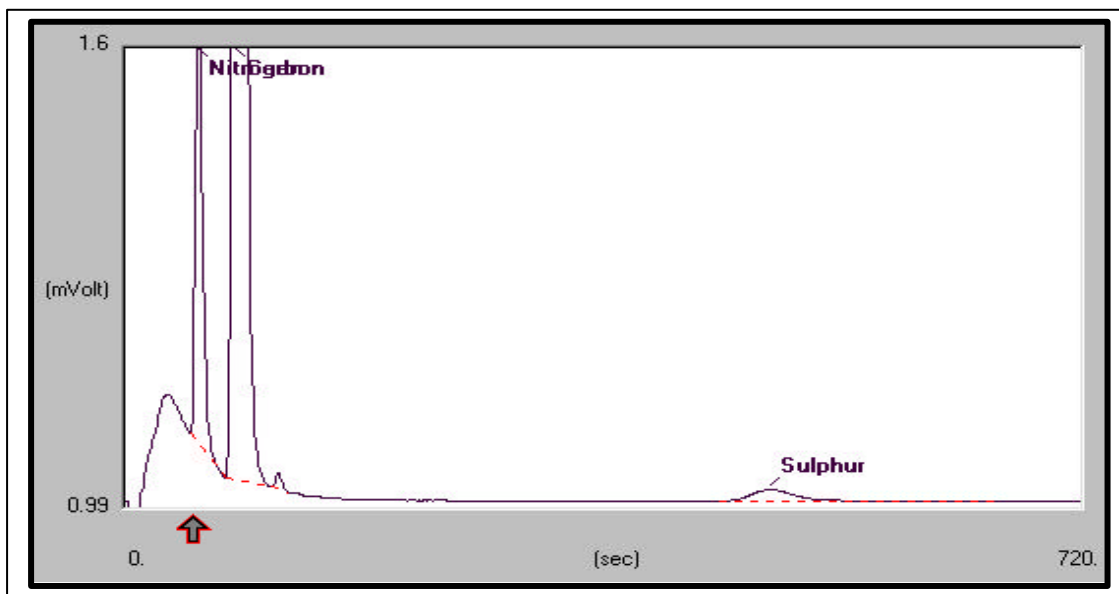
Typical CHNS chromatogram

**Chromatogram with a tailing on Nitrogen peak**

Chromatogram with a small peak after the Carbon peak.

How to establish the required amount of oxygen in CHN, CHNS and NCS configurations.

In the analytical conditions set in the page "Method" of the software Eager 300 there are two parameters that can be modified to optimise the method: one is the oxygen flow and the second is the oxygen injection time. The nominal values used are 250 ml/min and 5 seconds respectively.
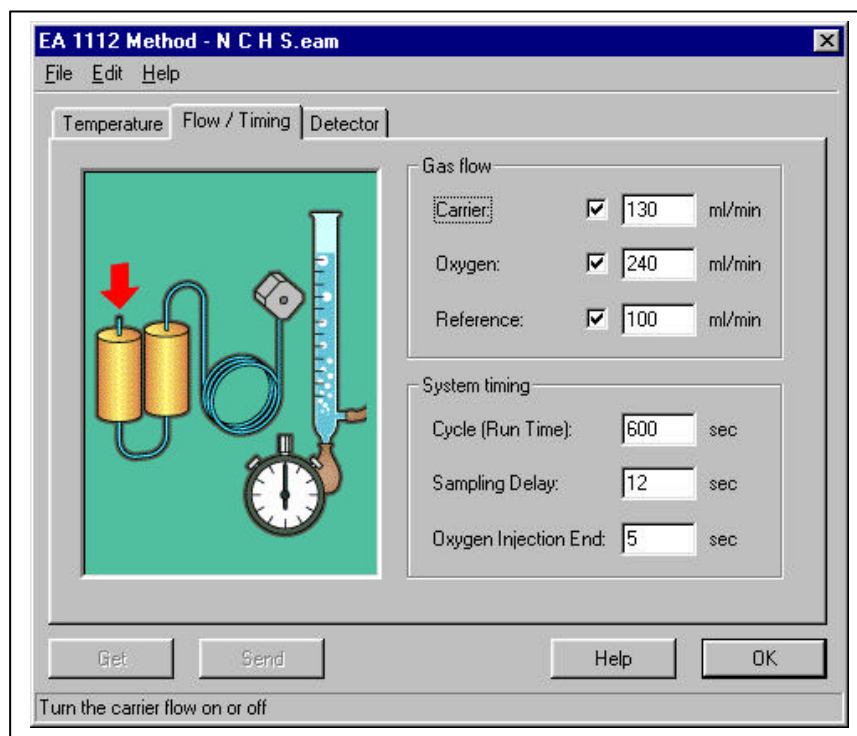
To establish the required amount of oxygen for a special application the following tests can be performed:

1) Modify the oxygen flow fixing the oxygen injection time, or
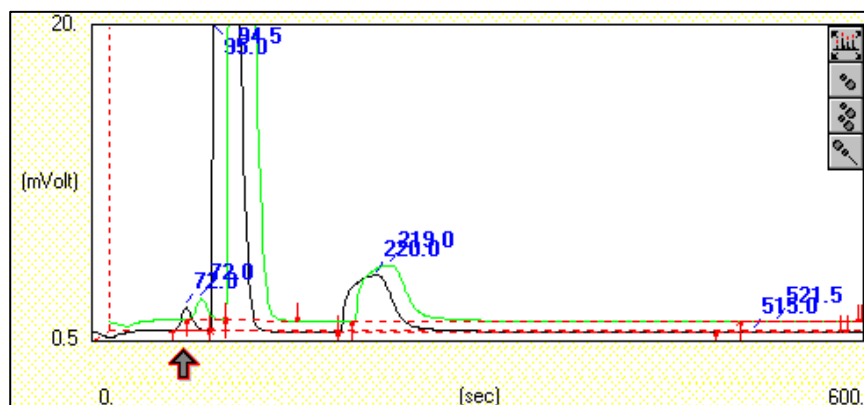2) Modify the oxygen injection time fixing the oxygen flow.

Note: *with possibility 1 there is no variation of the retention time of elements during the different runs while with possibility 2 there is a shift of retention times during the runs.*

Warning: *The calibration and analysis of samples must be performed under the same conditions of Oxygen flow and Oxygen Injection Time.*

Test 1:
   a) Run 1: Flow 300 ml/min, Injection Time 13 sec.
   b) Run 2: Flow 280 ml/min, Injection Time 13 sec
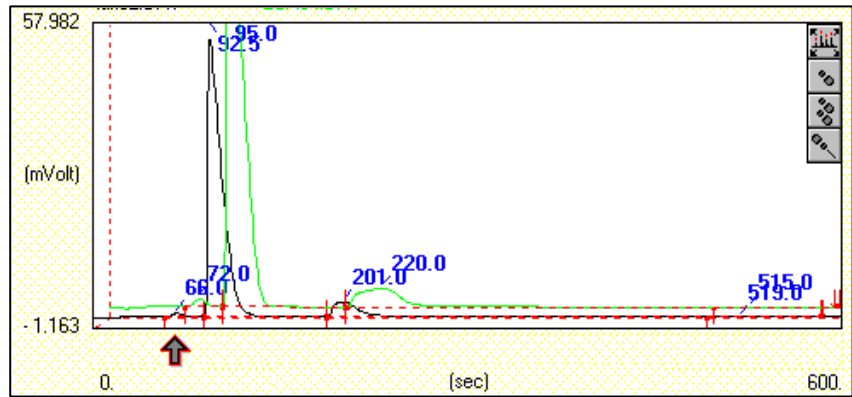
No variation of Retention Time of elements

Test 2:
c) Run 1: Flow 300 ml/min, Injection Time 6 sec.
d) Run 2: Flow 300 ml/min, Injection Time 13 sec

Shift of Retention Time of elements

Example of an analytical test for coke analysis.

It was modified the flow of oxygen and it was fixed the oxygen injection time. To perform this test it is necessary also to fix the weight of sample (for example about 3 mg).

The test consist in the analysis of 3 mg of sample as run 1 followed by a blank with a tin capsule as run 2 starting with the maximum flow allowed 300 ml/min and 13 sec as injection time for example. If the area of Carbon in the blank remain in the accepted values (10000-15000) indicated that the combustion of coke sample was complete, but it is possible that is too much oxygen free that uses the copper decreasing its lifetime.

The test will be repeated with lower flow of oxygen until the blank value is not acceptable (memory effect due to incomplete combustion of coke sample), indicating that the amount of oxygen used was not sufficient for this weight of sample.

The next table shows the different data obtained.

Test No.	Oxygen flow (ml/min)	Oxygen Injection Time (sec)	Weight of Sample (mg)	Blank C Area (mVolt)
1	300	13	2.984	12535
2	280	13	2.947	12860
3	260	13	2.996	11075
4	240	13	2.946	13728
5	220	13	2.973	39894
6	200	13	2.946	334444

The blank value increase when the flow is 220 ml/min or less. The best conditions for the analysis of about 3 mg of coke can be with a flow 240-260 ml/min.

Influence of Sample Delay on the combustion in CHN, CHNS, NCS configurations.

The nominal value used of Sample Delay in these configurations is 12 sec but sometimes for a few samples such as lubricant, oils is not correct for total combustion.
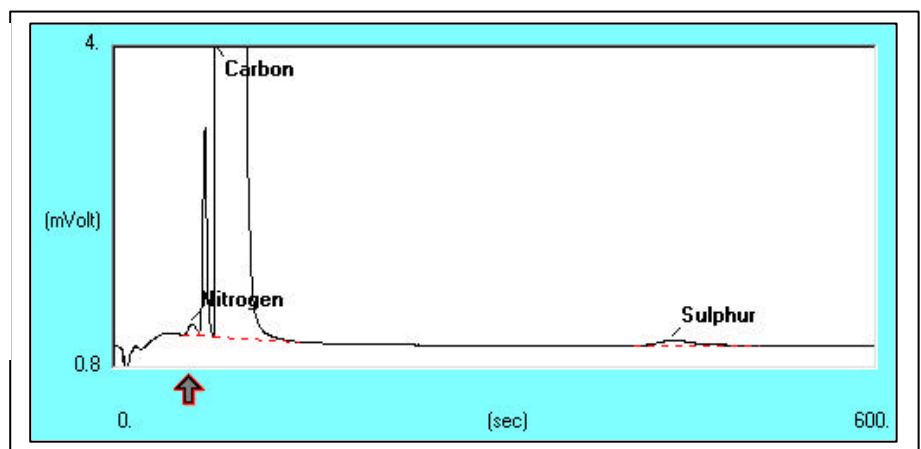
Trouble: In the chromatogram there is an other peak between Nitrogen and Carbon peaks.

Solution: Increase or decrease the Sample Delay until the extra peak disappear.
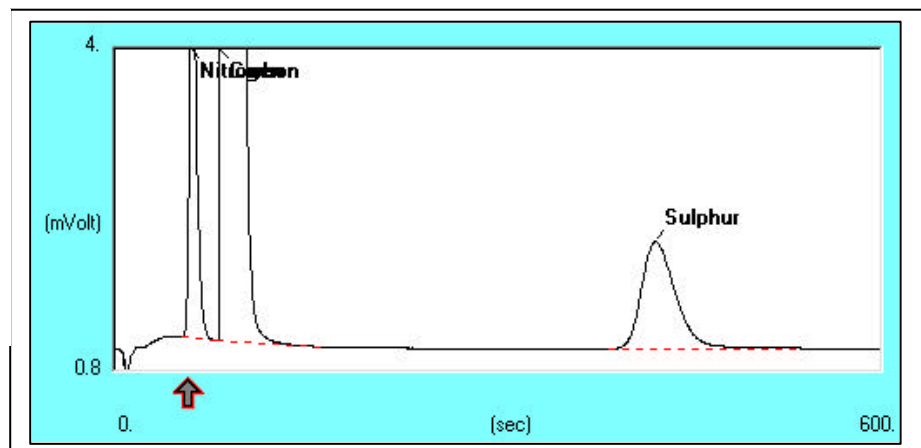
Test 1:

Sample Delay: 12 sec
(typical conditions):

Double peak for Nitrogen

Test 2:

Sample Delay: 15 sec
(new conditions):

Typical chromatogram

Bad combustion in Nitrogen / Protein configuration

The N/Protein analyser is an instrument designed for the macro determination of total Nitrogen present in a wide range of organic and inorganic samples. These include food, cereals, fertilizers, tobacco, feedstuffs, soils, beer and other materials which require characterization and quality control.

The combustion of the sample is the core of the analytical process. Reliable and reproducible results are obtained only if the combustion reaction is quantitative. A quantitaitve combustion is obtained only if the right weight of sample is dropped into the combustion reactor simultaneously with the correct amount of pure oxygen. When this condition is not satisfied, the combsution can not be complete: the chromatogram will immediately show a methane peak.

The combustion of some type of samples is not as easy as others: in particular, samples very rich in fats must be weighed in lower range or must be given more oxygen. The reason is found in the chemical structure of this type of sample: the fats contained in the sample consist of long aliphatic C-C chains, not easily combusted but easily cracked, with a high methane yield. The methane produced by the cracking is then partially oxidized by the oxidation catalyst, which is consequently partially reduced. So in this type of sample it is more likely, to have the methane peak eluted after the Nitrogen peak.

On the other hand, it is possible to increase the sample weight range or decrease the amount of oxygen required in the case of other types of samples: samples rich in water, for instance, are not difficult to combust.
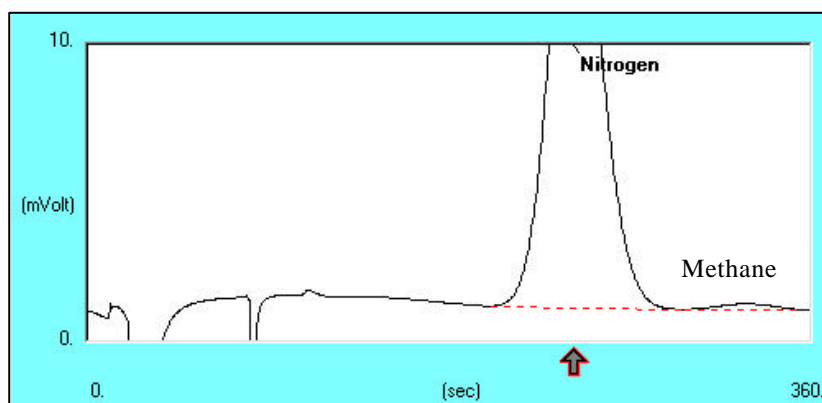
Typical N chromatogram

(Combustion OK)
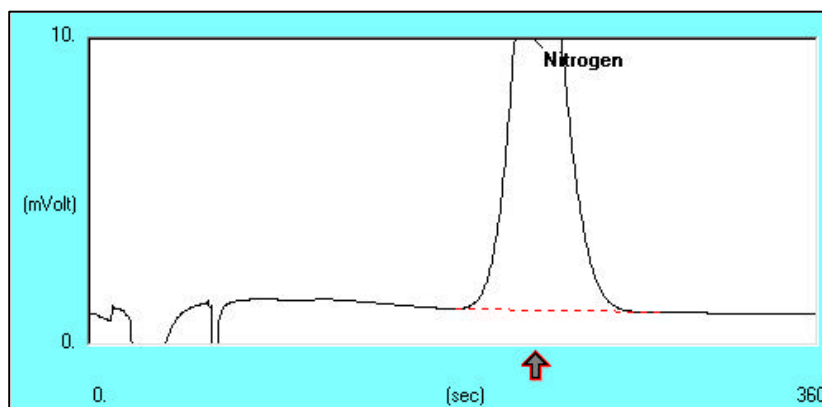
N chromatogram with bad combustion

(second peak: methane)

In conclusion a bad combustion is caused by one of the following reasons:

   a) too big sample size: can not be quantitatively combusted,
   b) combustion ashes: If the ash layer is too thick, the sample temperature is too low and is not enough for proper ignition,
   c) too little oxygen available : in order to perform a quantitative combustion, oxygen must be available in the right amount at the right time. If one of these two conditions is not achieved, complete combustion is impossible.

How to establish the required oxygen quantity in N/Protein configuration

There are samples that due to their nature require a minimum Oxygen quantity versus other samples that require greater Oxygen amounts. The software Eager 300 provides a Table comprising various categories where samples of different nature are memorized or can be memorized.

Selecting, after the weight entry, the category to which the sample belongs the system will deliver the right oxygen quantity required for a complete combustion.

Sample Table

Automatic Oxygen Dosing with the relative Category Table.

This condition is obtained by a feature provided thanks to the method below:

Method for Oxygen Dosage (OxyTune):

1) A fixed Oxygen flow of 300 ml/min was set.
2) The blank value was checked by repeat injecting Oxygen for 30 seconds in a resulting theoretical quantity of 150 ml.
3) Standardization was performed using aspartic acid (10.52 %N) from 50 to 100 mg and injecting fixed Oxygen amounts 30 sec.
4) Samples having different nature were analysed as follows:
   a) 200 mg of sample and 60 sec Oxygen Injection Time .
   b) At the end of the analysis the blank was run again.
   c) The same procedure (sample analysis and subsequent blank analysis) was followed reducing the injection time at every sequence run. Checking the increased blank value, the combustion critical point was established.
   d) After having established the combustion critical point, the ideal Oxygen/sample weight factor (obtained dividing the Oxygen quantity injected by the sample weight) was found and stored in an appropriate category.
   e) The sample analysis was repeated starting by reducing the weight to 100 mg and then increasing the weight until reaching the maximum quantity accepted by the container. Being ideal factor multiplying value memorized, the Oxygen amount for each single analysis was automatically calculated simply selecting the category the sample belongs to.

Based on these results the Table shown before was created.
This Table contains:
- Four categories for samples A, B, C, D where the ideal factor values (Oxygen/sample weight-sample nature) of the samples have been prefixed.
- The nature of samples.
- Four free categories E, F, G, H where sample names not considered in categories A, B, C, D can be memorized. When a free category is selected, the ideal factor value must be entered in the appropriate box.

Ideal Factor Value:
Correlation between Oxygen and Sample weight/nature.
For category A, B, C, D an ideal factor value was fixed:
Category A: 1.3
Category B: 1.1
Category C: 0.4
Category D: 0.2

In the categories E, F, G, H, were included other samples. For example for chocolate (category E or F) was used 2.2 or 1.4 as factor depending of type and weight of sample used.

Influence of exhausted consumables on the analysis.

1) Influence of exhausted Copper.

In all configurations the function of the Copper is to reduce the Nitrogen Oxide to molecular Nitrogen, to reduce Sulphur Trioxide in Sulphur Dioxide and to retain the excess of Oxygen used for the combustion. During these redox reactions the Copper is converted in Copper Oxide.

Troubles: Bad separation between Nitrogen and Carbon
Increasing Nitrogen blank value.
Increasing in the Nitrogen data.

Solution: Replace the reactor.

Example: NC chromatograms where the Copper is exhausted:
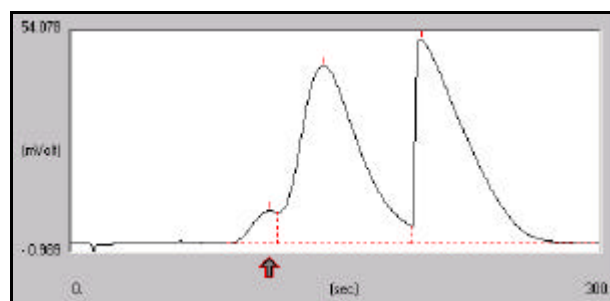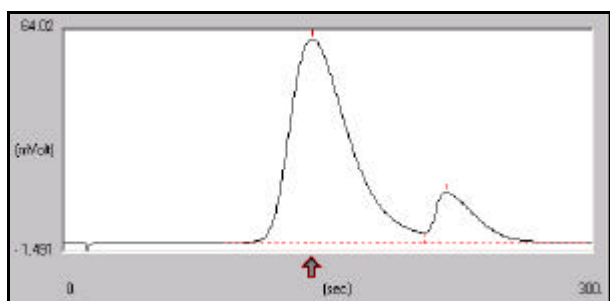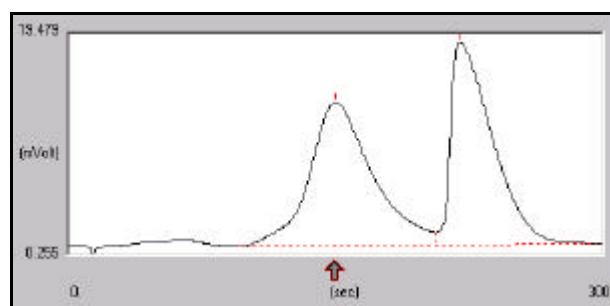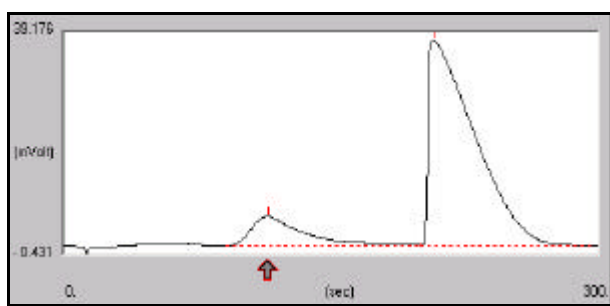
2) Influence of exhausted Soda Lime

In N/Protein configuration the first trap is filled with Soda Lime that retains the Carbon Dioxide produced during the combustion and also part of the water produced.
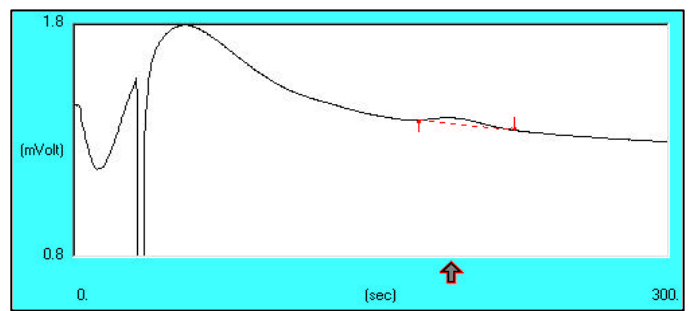
Troubles: Increasing in the Nitrogen % data
Tailing in the beginning of the Nitrogen peak
Bad Nitrogen Blank chromatogram

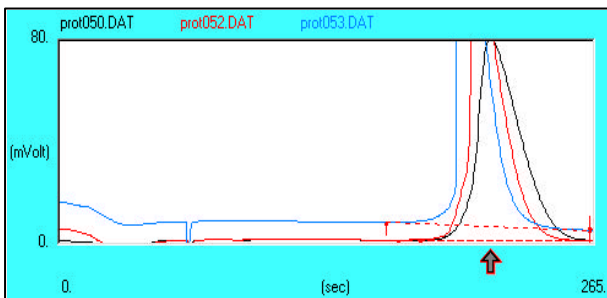**Solution:**   Change the Soda Lime.

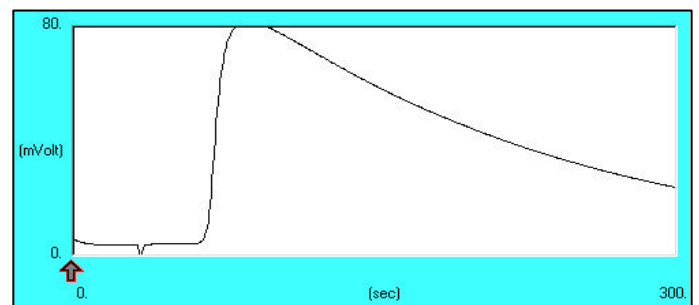**Typical Nitrogen chromatogram**
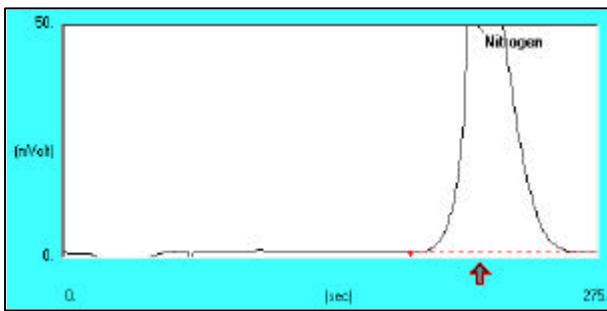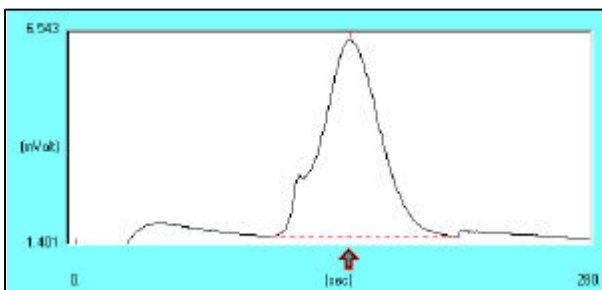

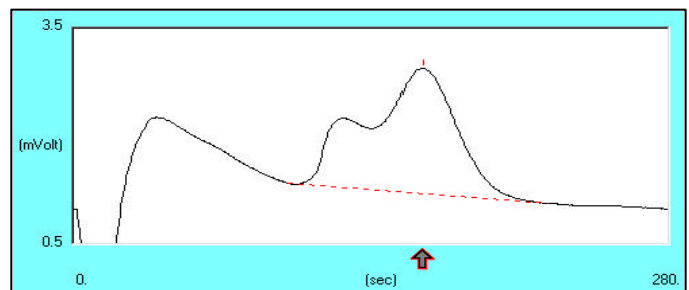**Typical blank analysis**

Tailing on Nitrogen peak

Bad Blank analysis

Tailing in the start of the peak

Double peak

3) Influence of exhausted Anhydrone.

In NC and N/Protein configuration the trap filled with anhydrone is to retain the water produced during the combustion of the sample.

When the anhydrone is completely wet it may produce an obstruction in the trap and consecutively a decreasing in the Helium carrier gas flow.

Troubles: Retention times deleted respect to the typical chromatogram.

Solution: Change Anhydrone.

Analytical Troubleshooting related to sample nature:

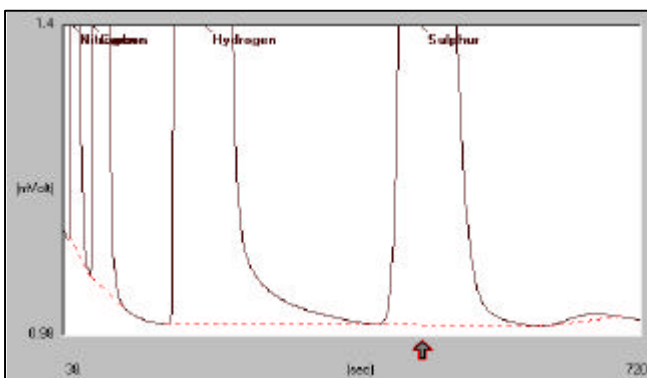### 1) Tailing or split of Sulphur peak: Incomplete conversion of Sulphur

Troubles: Tailing of Sulphur peak
Double Sulphur peak.
Bad reproducibility and accuracy of Sulphur data.

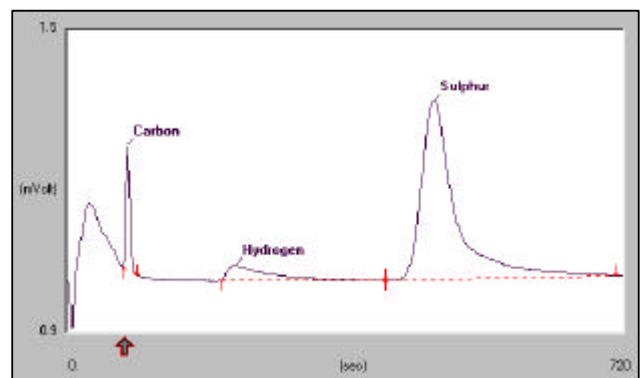**Solution:**   Add about 10 mg of Vanadium pentoxide into the tin container when weighing the sample.

Typical CHNS chromatogram.
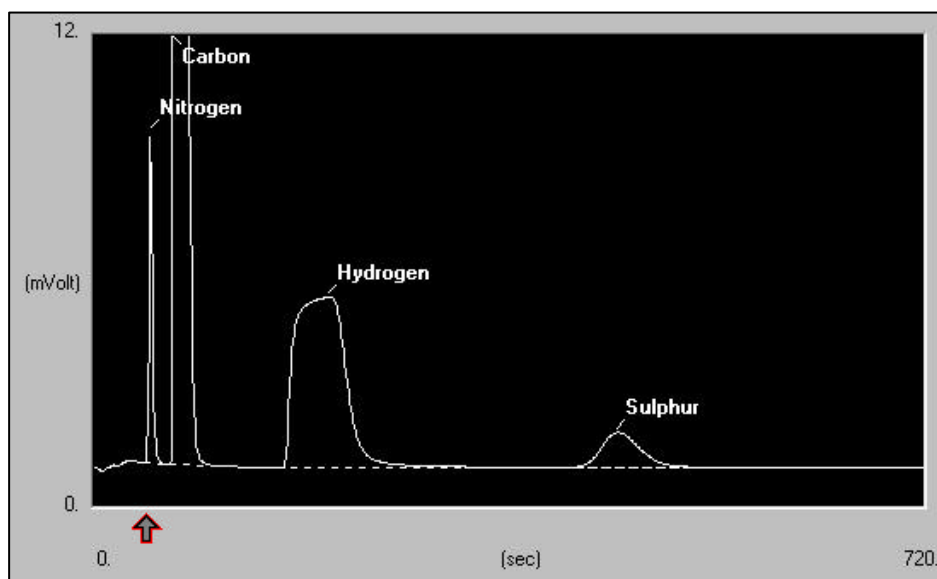
Double Sulphur peak

Tailing on Sulphur peak

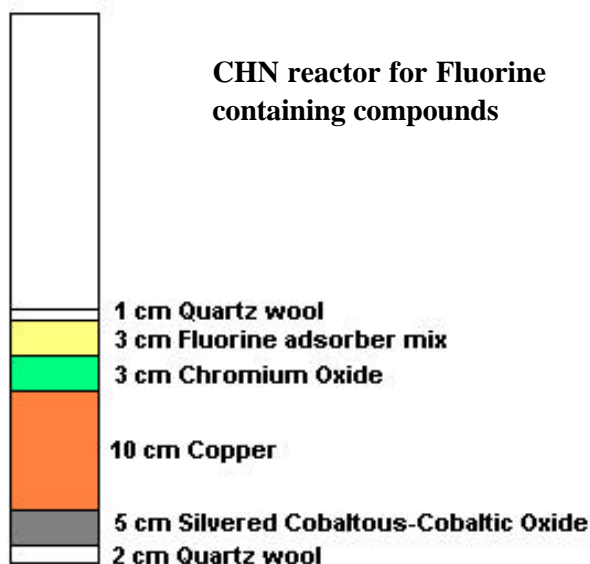## 2) Split on Hydrogen peak: Presence of fluorine containing compounds.

The analysis of Fluorine-containing compounds shows many difficulties due to the high reactivity of this element. Other halogen atoms (Cl, Br and I) do not influence CHN / CHNS determinations, no specific precautions need to be taken.

Troubles: Tailing or splitting on Hydrogen peak
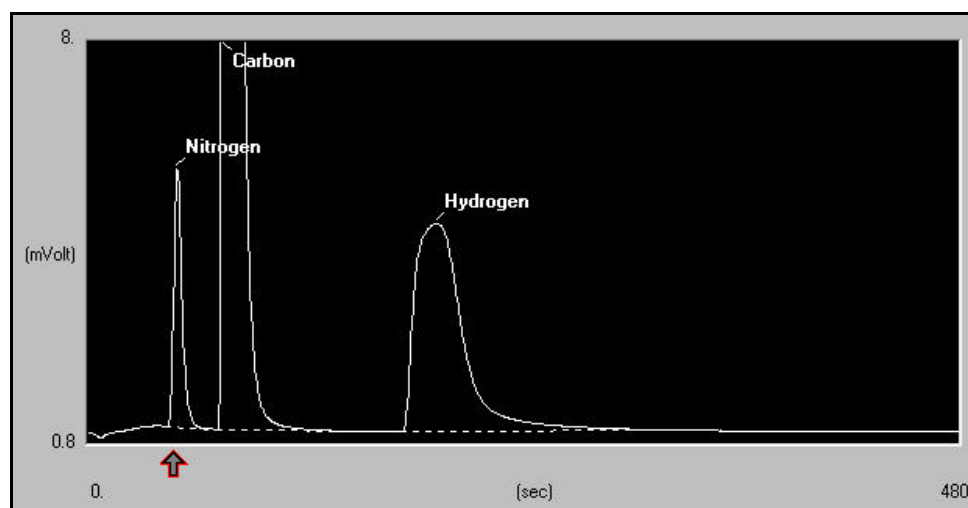   Ghost peaks on Carbon peak

Solution: **For CHN configuration**: to eliminate the problem fill a reactor with the specific
            absorber Fluorine mix (according with the relative layout, see below).
             For CHNS configuration: to reduce the problem, weigh 0.4-0.6 mg of sample in a
            Silver capsule (P/N 24005405).

Analytical conditions

T tube: 950°C
T oven: 75°C
Helium Carrier Flow: 140 ml/min
Helium Reference Flow: 100 ml/min
Oxygen Flow: 250 ml/min
Oxygen Injection Time: 5 sec
Sample Delay Time: 12 sec
Total Run time: less than 8 min
Standard: Acetanilide 0.8-1.2 mg
Calibration method: K factor
Sample weight: 0.8-1.2 mg

CHN reactor for Fluorine containing compounds

1 cm Quartz wool
3 cm Fluorine adsorber mix
3 cm Chromium Oxide
10 cm Copper
5 cm Silvered Cobaltous-Cobaltic Oxide
2 cm Quartz wool

Typical CHN chromatogram

CHN chromatograms of Fluorine containing compounds: Effect on Hydrogen peak
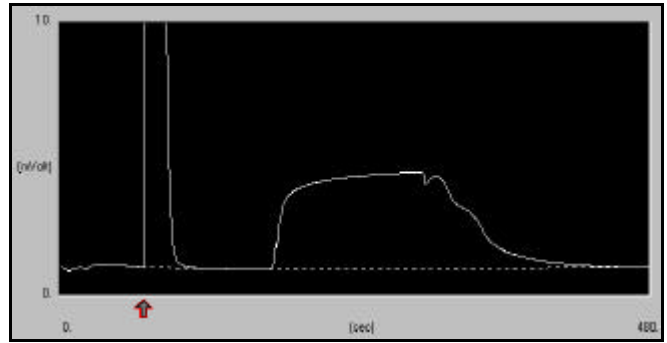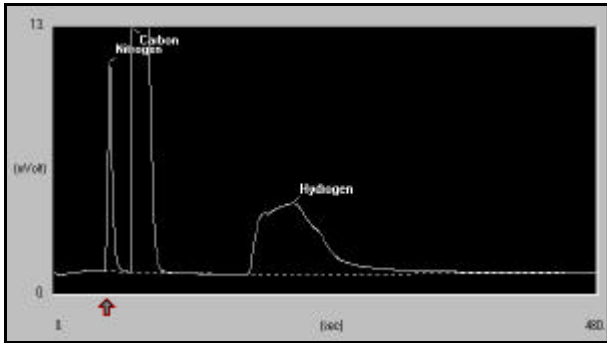
CHNS chromatograms of Fluorine containing compounds: Effect on Hydrogen and Carbon peaks.