

Ambient measurement at ppt-level: the Syntech Spectras GC955 butadiene-benzene analyser

Introduction

Regulations for benzene on the EU-level

Problematic for the measurement of benzene and butadiene in ambient air

Measurements in the UK for butadiene

Measurements in Italy for butadiene

Introduction

In the ambient air generally only a few carcinogenic hydrocarbons are found. Benzene is the main component, butadiene and formaldehyde are present in lower concentrations. To evaluate the effect of the European strategy for diminishing the concentrations in the ambient air to safe levels, the study of these is important. Our company has been involved in the measurement of low concentrations by automatic gas chromatographs in situ for benzene since 8 years. During the last two years several trials with equipment that can include butadiene were set-up. We now present an instrument that can measure butadiene well below the 10 ppt level with certain identification.

First I will give some information about the European regulations and the resulting measurement strategies concerning benzene.

Problematic and solutions:

The measurement of benzene in ambient air is not very difficult. Trapping on several materials is possible. In the separation care has to be taken to avoid coelution with cyclohexane, tetrachloromethane and 1,2dichloroethylene. In rural background situations the levels have sunken below 0.1 ppb. This means that equipment must be extremely sensitive and linear down to the lowest range.

The measurement of butadiene in ambient air is very difficult:

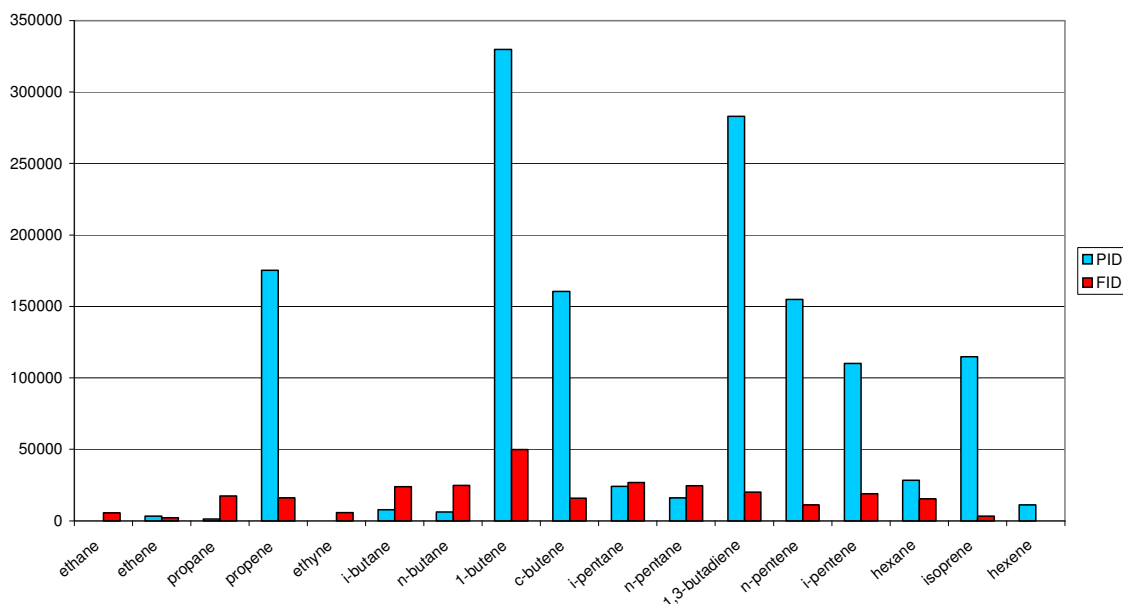
1. The reactivity is high and the sample must be analysed before reaction with ozone has taken place.
2. Concentrations are in general below 0.1 ppb
3. The boiling point is low, and trapping must be done on selected traps.
4. Together with butadiene other components are found with similar boiling points at much higher concentrations. These can easily be confounded with butadiene and misidentification must be excluded.

To avoid reaction in the sample we first worked with a cooled trap. We find however a good response for butadiene now by trapping on Carbopack B at ambient temperature. As this trapping takes place at low flow during the 12 minutes before injection, reaction with ozone and radicals will be limited. However a study to this phenomene should be undertaken using mixtures with and without ozone.

To reach the required sensitivity we use a photo ionisation detector. This detector is especially sensitive to butadiene. See below data concerning the relative

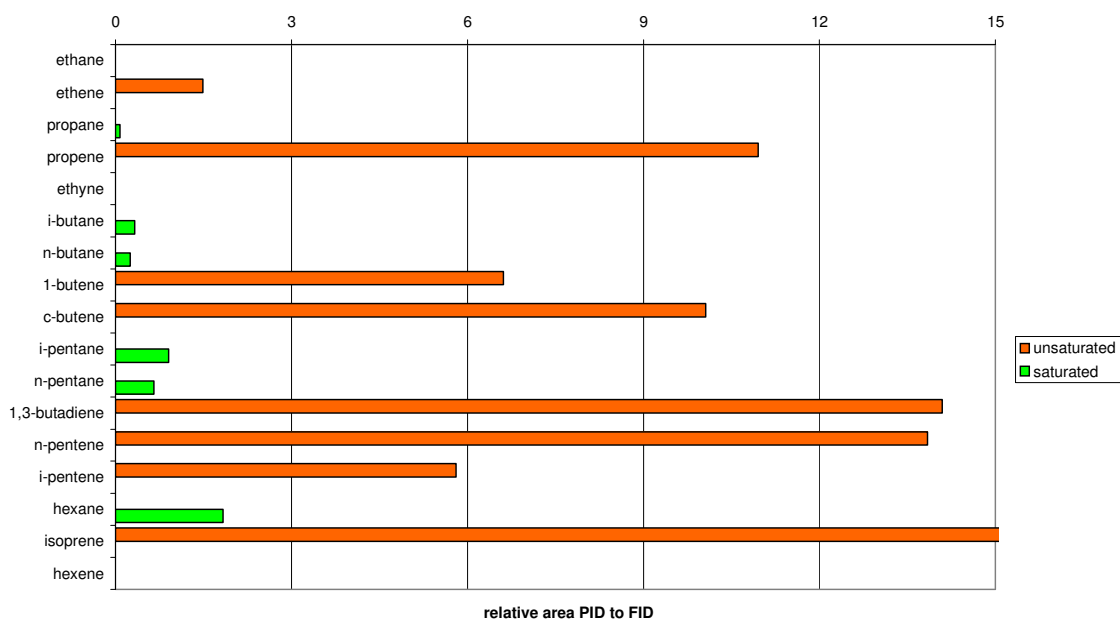
sensitivity of a PID compared to an FID for the C₄ components n-Butane, iso-Butane, iso-Butene and cis-Butene and lastly for Butadiene. It is clear that the PID is the best detector that can be used for this.

Comparison PID to FID for C₂ to C₆ hydrocarbons



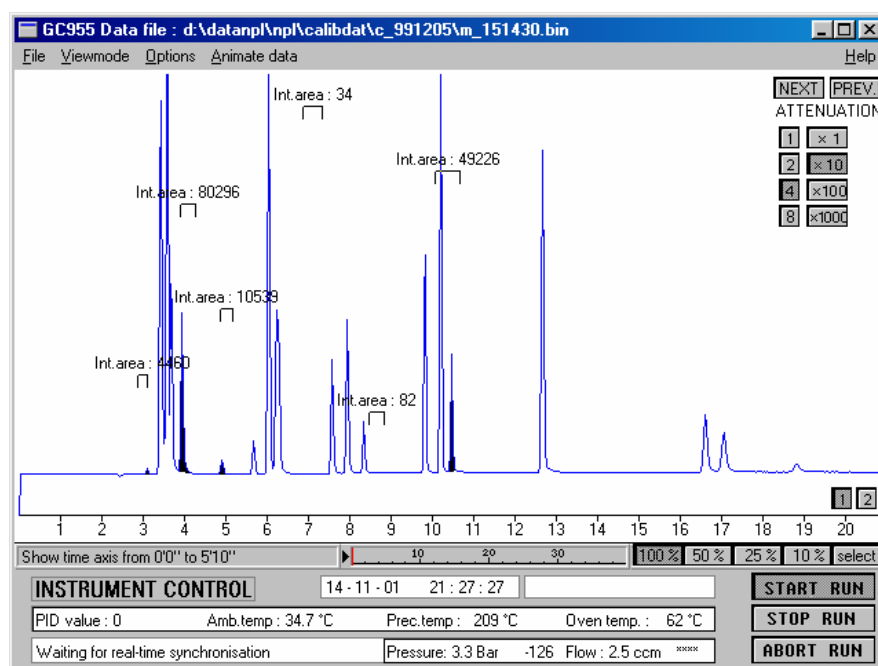
Area of measurement for C₂ to C₆ hydrocarbons (no benzene). Trapped on a cooled Carbosieves preconcentration, desorbed at 250 °C and separated on an Al₂O₃ column. Concentrations from ca. 1 to 10 ppb.

Comparison sensitivity of PID and FID for C₂ to C₆ hydrocarbons

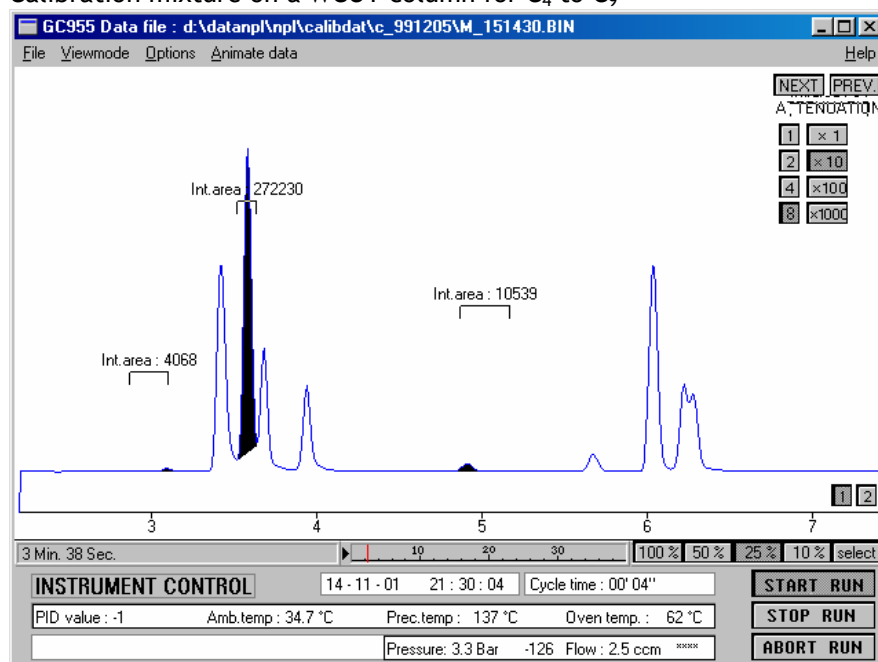


Relative area from the measurements in figure xx. Ethane, propane and ethyne not measured on PID, hexene not on FID. The sensitivity for the saturated hydrocarbons is about the same for PID and FID above C₄. The sensitivity of the PID to alkenes is about 5 to 15 times higher as that for the FID for the same components.

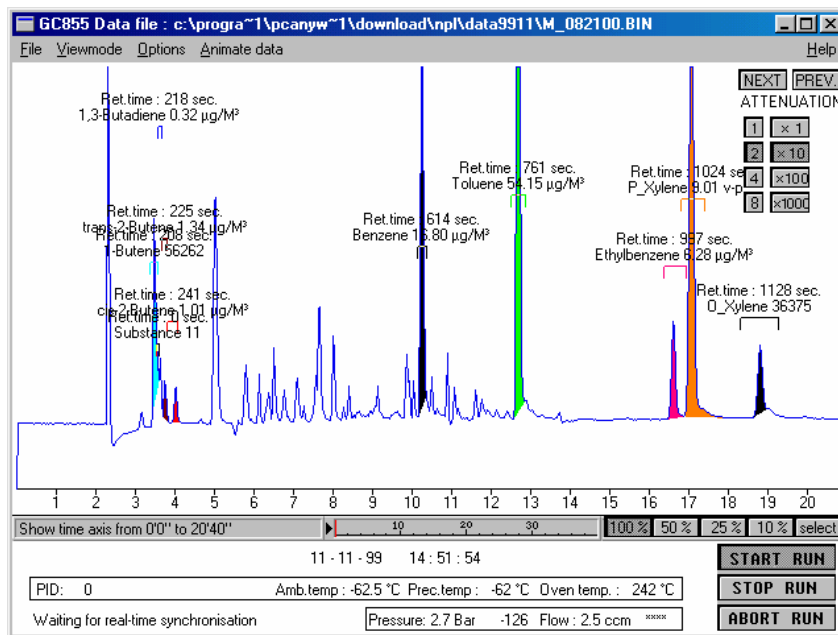
Our original solution for the separation problem was a long conventional WCOT column with a thick film and a temperature program starting below the normal minimal range of 40 °C. Cooled down to 20 °C we were able to separate butadiene from the C₄-components. In the field interferences from oxidised hydrocarbons, leading to broad peaks disturbed this measurement. This led to a minimum detection limit in practice of ca. 0.02 ppb. This was too high for the field.



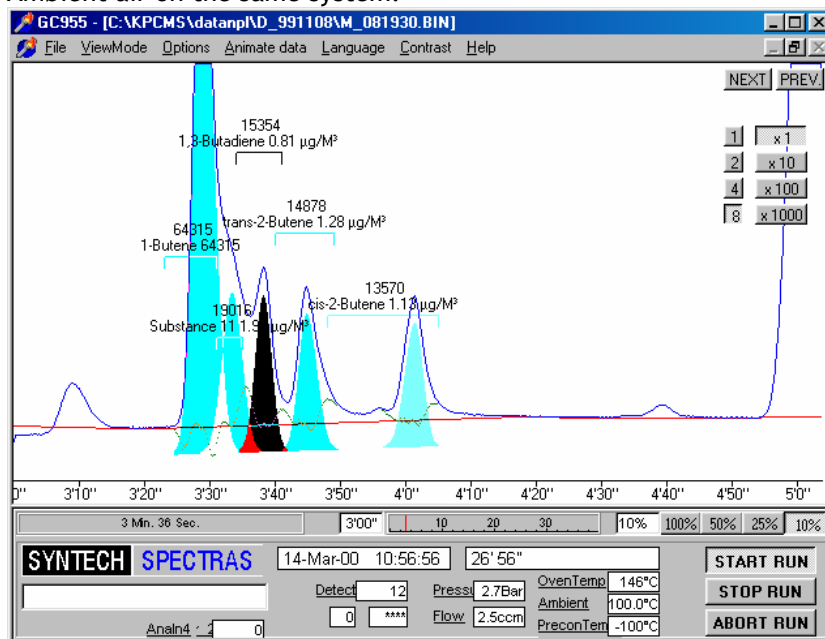
Calibration mixture on a WCOT column for C₄ to C₉



Enlarged chromatogram for the C₄: butadiene is integrated



Ambient air on the same system.



Enlarged chromatogram for the C₄ components: substance 11 was not present in the calibration mixture and influences the measurement of the butadiene.

In our present solution we no longer use a WCOT but a PLOT column. We choose to use a Al₂O₃ column. The consequence was that we no longer measure toluene and xylenes. The reasons are two: first of all the analysis time would become very long. In our small GC the oven cannot be heated up to the max. temp of the column. The second is however that we do not want to inject any water unto the column. Al₂O₃ columns are infamous for their shifting retention times. In our view this is mainly caused by the water in the sample. This water effect was the reason, chromatograms of the VOC-air, used in several networks, had to be retreated with a view to their retention times.

With a short precolumn of WCOT, and only injecting up to benzene (BP 80 °C), we do not see the water effect. After installing a system and setting to work, the retention times shift for up to 50 hours. Then the system stabilises and works continuously on.

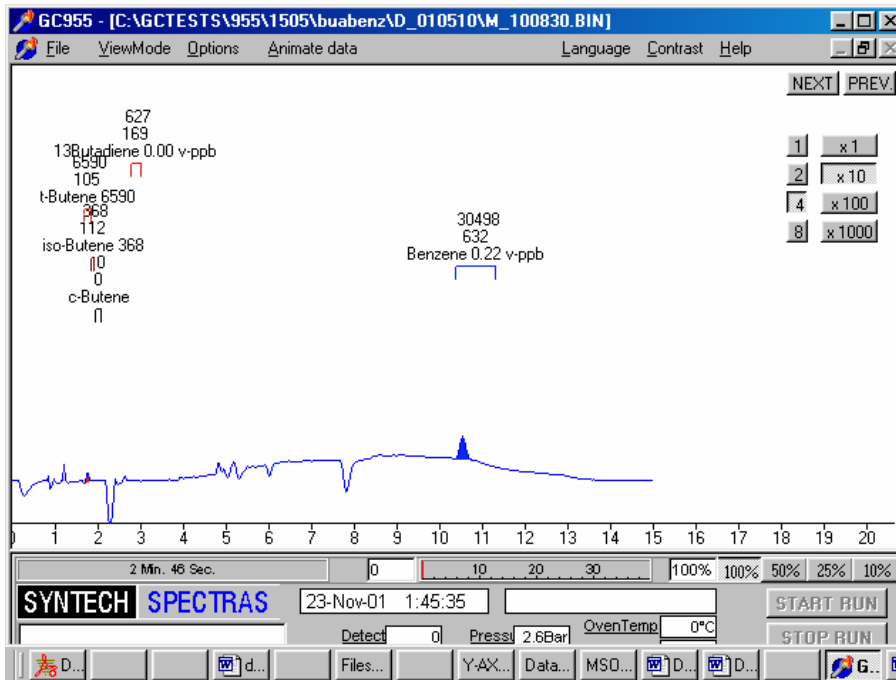
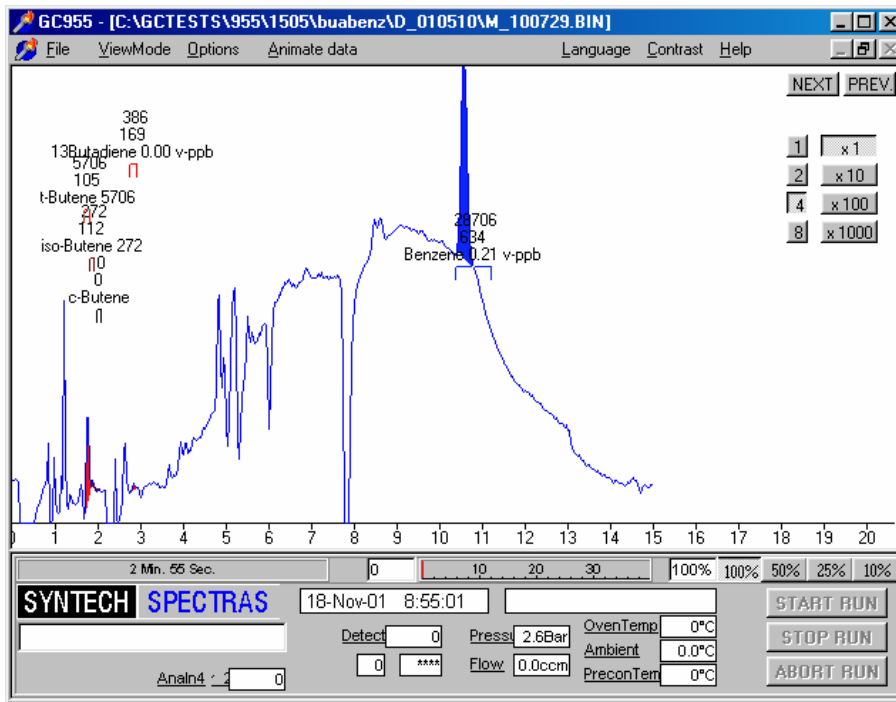


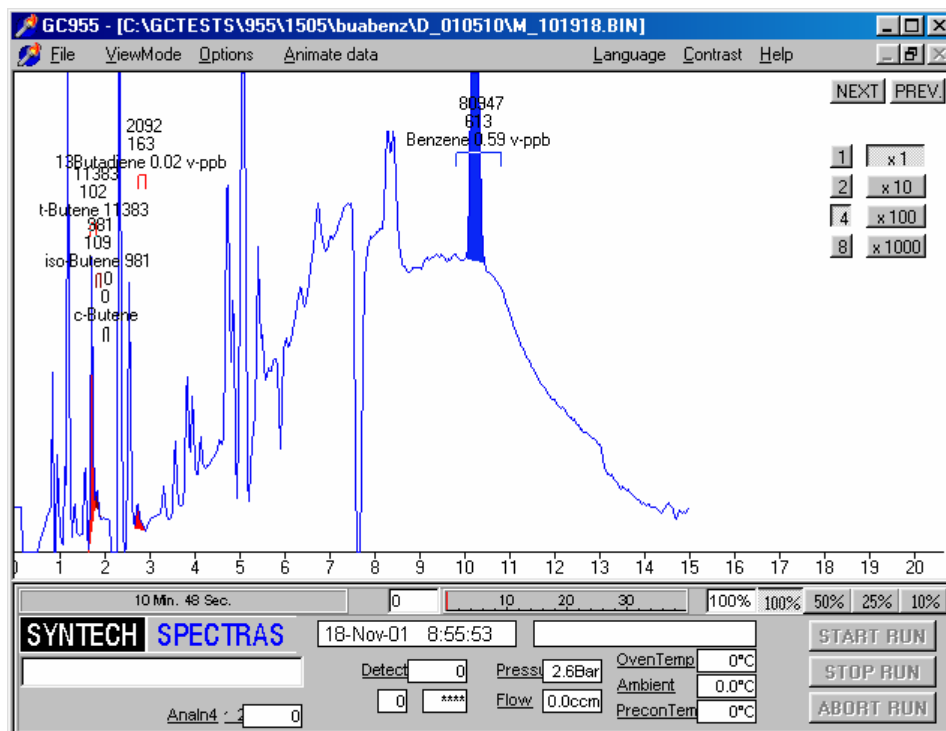
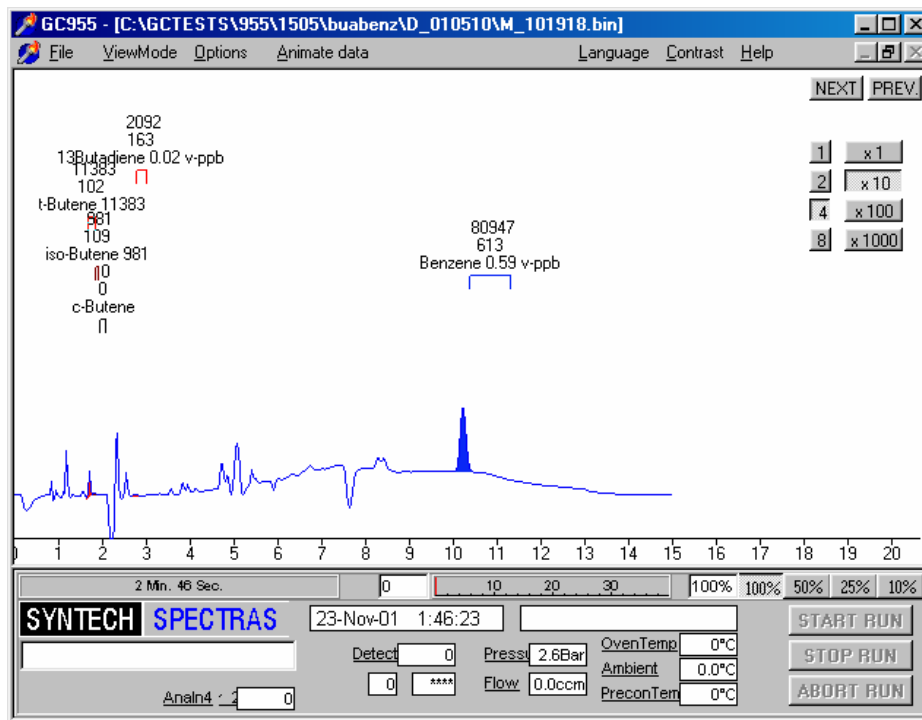
*Gas chromatograph opened with oven at the right top.
Still missing;
(Photo of the small oven and photo of the double column in it)*

The system as it is working now, was first tested at the site of AEA in May of 2001. The instrument was installed at the basement of a building away from any direct traffic influence. It worked without problems, however the butadiene concentrations were really low at this background site in mild spring weather in the UK.

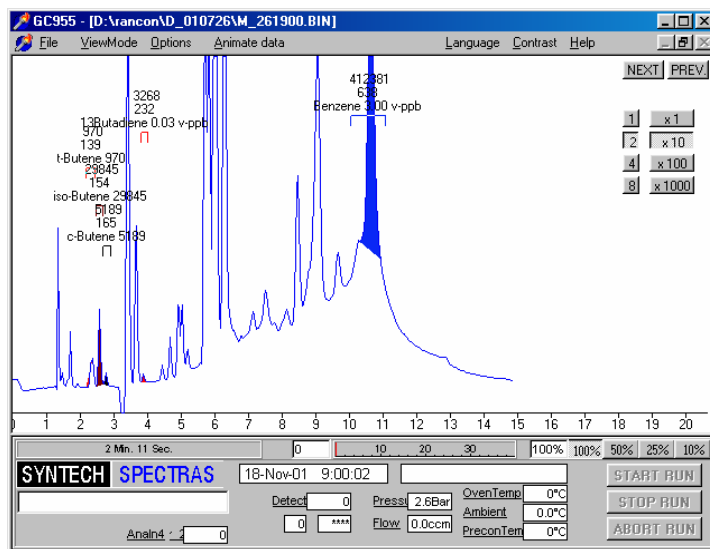
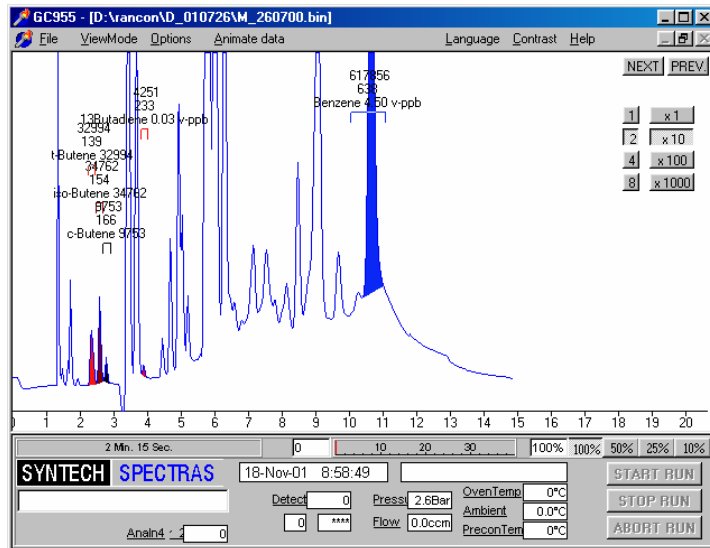
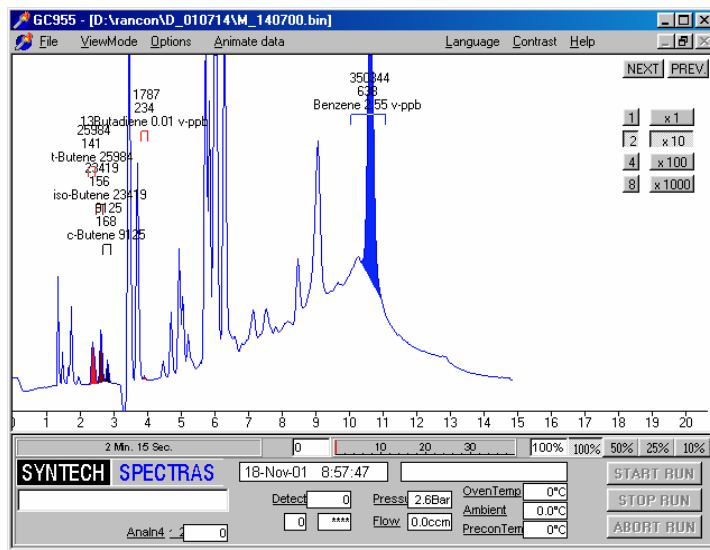
A second test was made in Milano in Italy during the high summer and the early winter. Here we installed the instrument in the middle of the city. It was however installed at the second floor of a building and the distance to direct traffic was about 100 m on all sides.

A typical chromatogram of all three periods is shown: for Harwell very flat, for Milano in summer quite depending on the daytime, for the winter less.

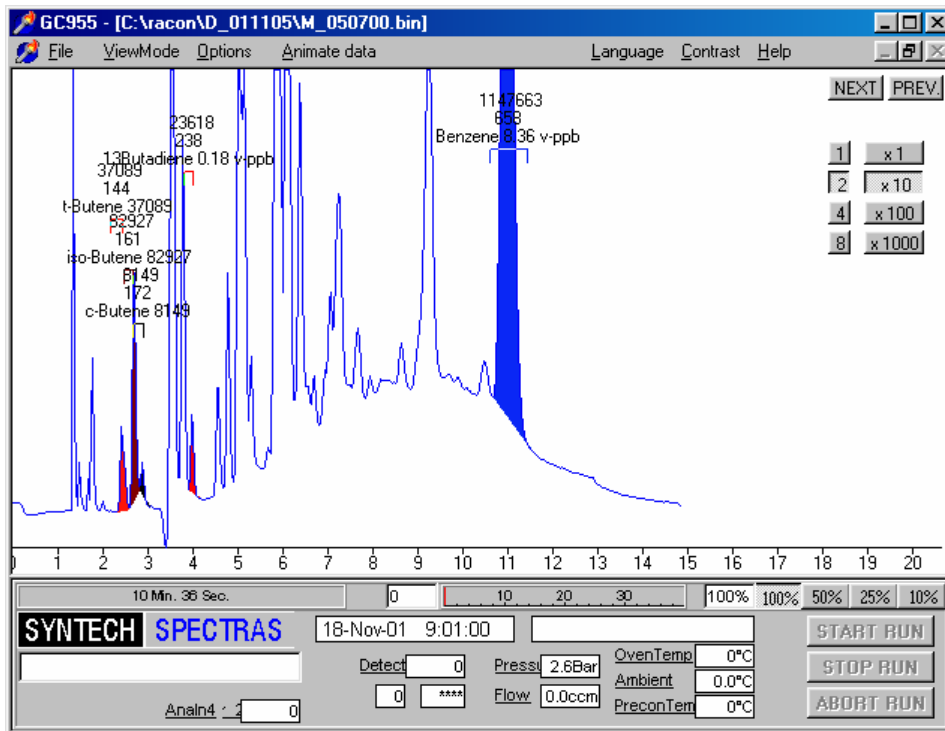
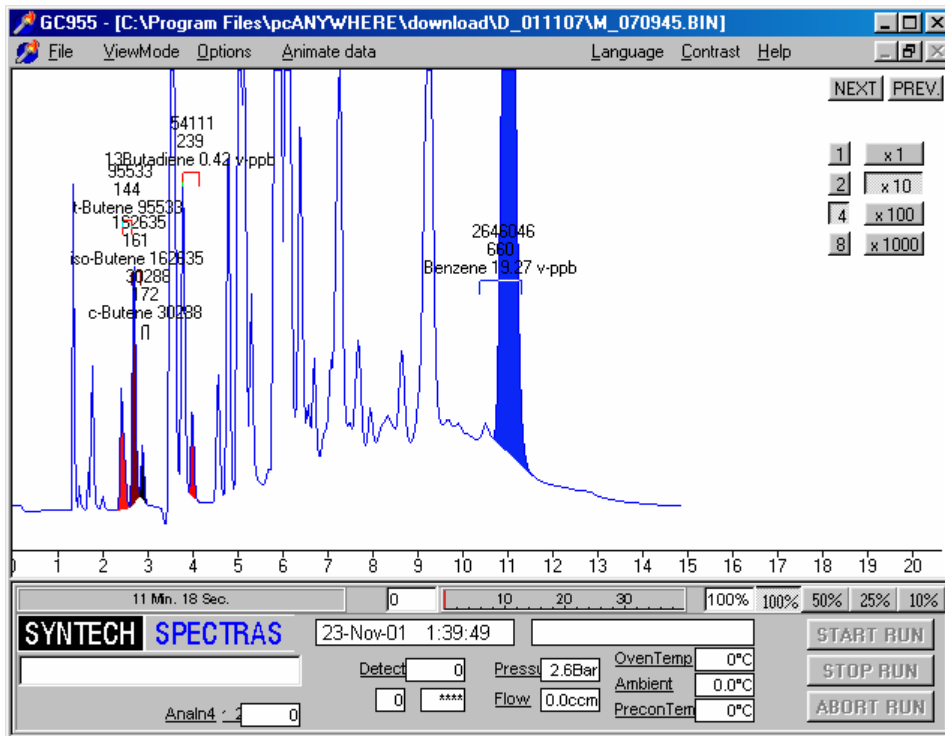


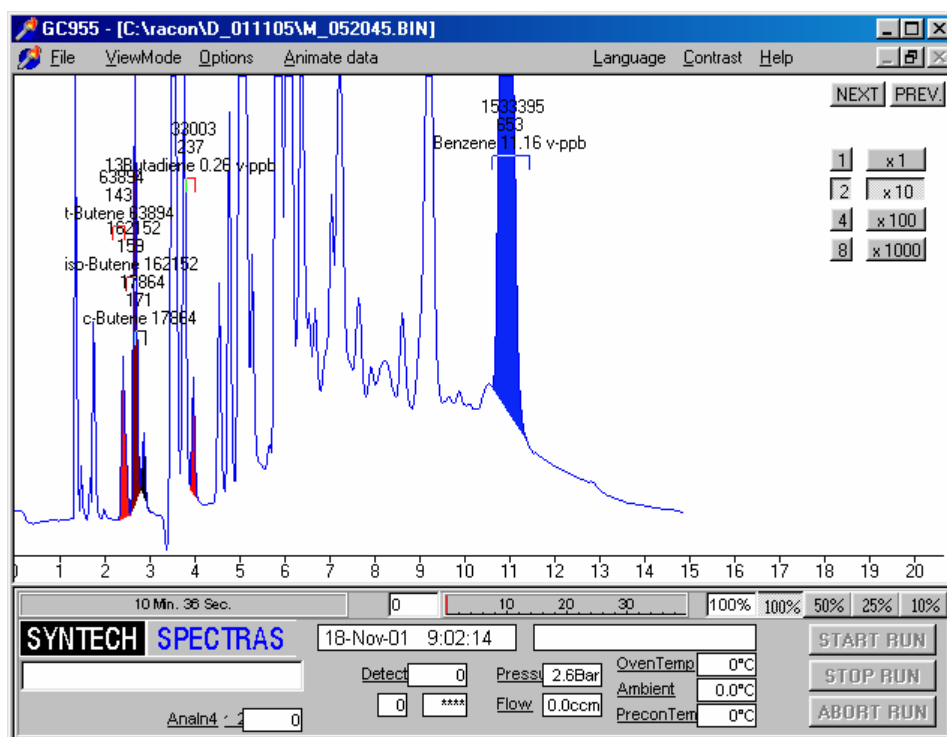


Harwell may 2001



Milano July 2001





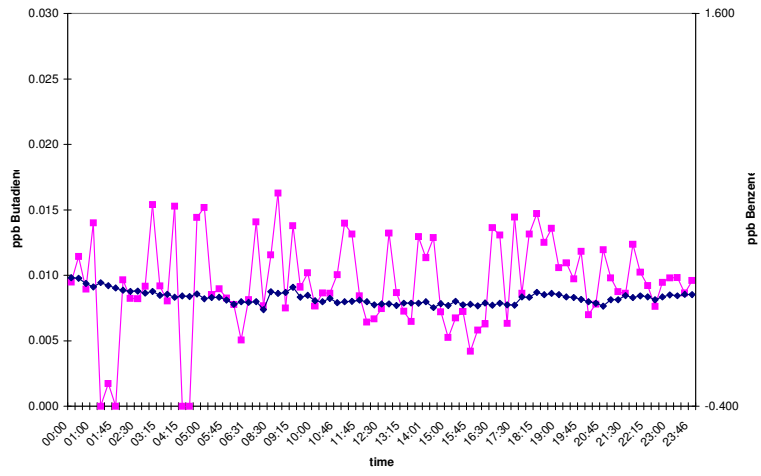
Milano, november 2001

The daily variation was as expected lowest in Harwell.

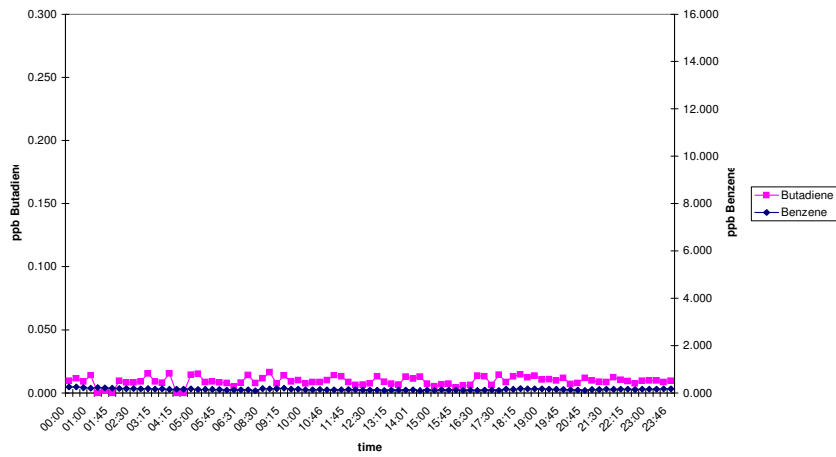
In the high summer in Milano the concentration of butadiene showed quite clearly the influence of the ozone smog: the concentrations rose in the morning and then sharply dropped. At the same time the concentration of benzene stayed higher. In city summer smog the ozone smog is only very slowly destroyed during the night. The concentration stayed very high.

In the winter period in Milano the first thing to be noted was the really high benzene concentration. This is an indication of the vehicle emission, influenced by an inversion situation that is already in november formed easily. The butadiene concentration was also much higher. Quite new is the situation, that the concentration is highest not during the day, but late in the evening. When the daylight period is short, the ozone smog formation period is also shorter. Obviously at the end of the day during the evening rush hour (that goes on very long in Milano, as people arrive already late after their long morning trek) the butadiene that is emitted is no longer reacting with the smog but accumulates in the boundary layer.

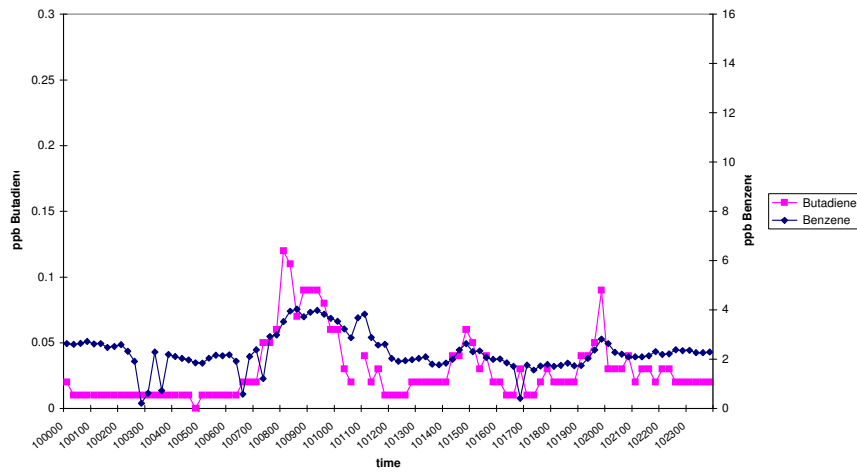
Benzene and Butadiene at Harwell, May 17 2001



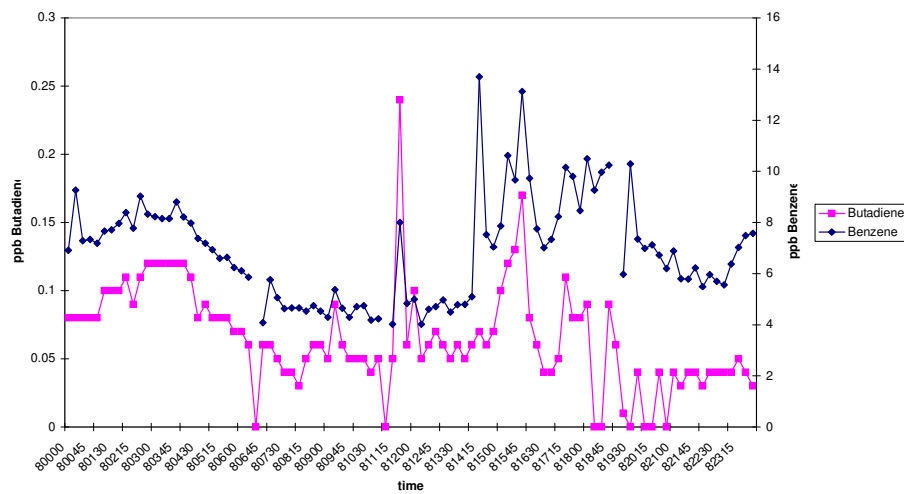
Benzene and Butadiene at Harwell, May 17 2001



Benzene and butadiene on July 10, 2001 in Milano



Benzene and Butadiene on November 8 2001 Milano



Interesting is the ratio of butadiene to benzene. *It is for Harwell about 1:100, for Milano about 1:80*

Conclusions:

1. The measurement of ambient air hydrocarbons is an exercise in minimalism.
2. The Syntech Spectras GC955 is up to these levels and can face the separation problems for benzene and butadiene both.
3. However in this solution we lose the xylene. We get back however the opportunity to study the other C₄, C₄ and C₆ hydrocarbons: this opportunity should be used, as it is a good part of the reactive ozone hydrocarbons.
4. Realistic testing of such equipment should contain tests under ozone smog conditions.
5. The ratio of benzene to butadiene is very high.

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Synspec, Groningen , The Netherlands, november 2001