

Measurement in situ of ozone precursor components near an industrial zone with an automatic double gas chromatograph

Titia Meuwese-Mulder, Synspec, The Netherlands, November 2001

Introduction:

The Ozone concentration in the troposphere in the summer is one of the main concerns in European air quality.

The factors leading to this phenomenon are well studied: the combination of radiation, temperature, nitrogen oxides and hydrocarbons leads to a cyclic process in which during the step-by-step degradation of the hydrocarbons to oxidised end products much ozone is formed.

Many model studies have been performed. As the radiation and the temperature are natural phenomena, human intervention is only possible with the nitrogen oxides and the hydrocarbons. It has been shown that removal of the nitrogen oxides only will not lead to a large decrease. Removal of the hydrocarbons from the atmosphere is not easy. Where the main sources of the nitrogen oxides are the burning of fuel for energy production, either in vehicles, in electricity production or in house heating, the source of the hydrocarbons is more diffuse and thousands of different components are emitted.

Main sources for the hydrocarbons are: traffic, natural sources, industrial processes, various household products.

As a result of the model studies in Europe 32 components that are the more important ozone precursors have been listed. These are selected both for their reactivity as for their concentration in the troposphere.

Measurement method

Measurement of these hydrocarbons is mainly done by two techniques: first sampling in canisters and then later analysis in the laboratory. And second sampling and analysis directly in the field. The problem with the canister, the first method is that many of the important ozone precursors are reactive and may already react before measurement. Ozone scavengers during the trapping will help. Also the canisters cannot be used for a longer period at great resolution. The second method, with direct analysis in the field can only be performed with specially adapted instruments, like the set-up shown here.



Instrumentation

Synspec has been developing since several years equipment for the trapping and measurement of hydrocarbons in the field. Since 1999 we are working on the improvement of gas chromatographs for the

POCP measurement. The instrument consists of two gas chromatographs, each with their own trap. The low boiling hydrocarbons (C2 to C5) are trapped at 5 °C on a Carbosieves trap, with a Perma Pure dryer in the sampling line. They are analysed on a short aluminium oxide column with an EPA-624 equivalent precolumn.

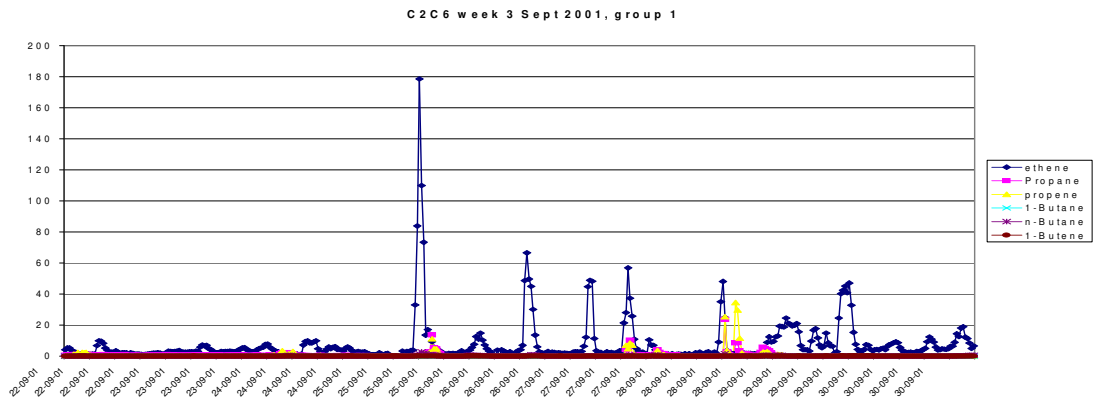


The high boiling hydrocarbons (C6 to C10) are trapped on Tenax GR and analysed on a EPA-624 equivalent column. To improve identification of the components, in the low boiling instrument two detectors are used: a PID and an FID. Both gas chromatographs are equipped with mass flow controllers and mini diaphragm valves.

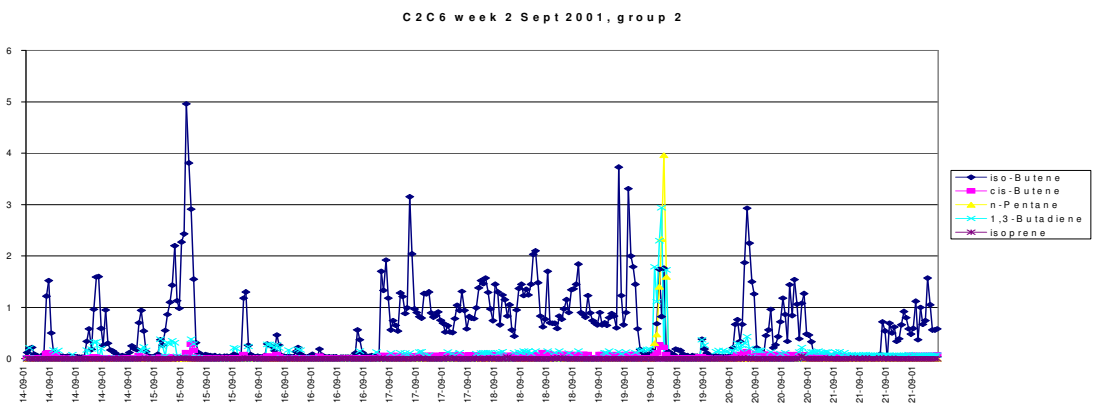
The instrumentation is self-starting, the internal PC saves the chromatograms and the measured and calculated concentrations on the hard disk. Communication options with RS232, ethernet etc. Calibration with low concentration multi-component mixtures (NPL) for 27 components.

Results of a test near an industrial zone with an in situ measurement instrument:

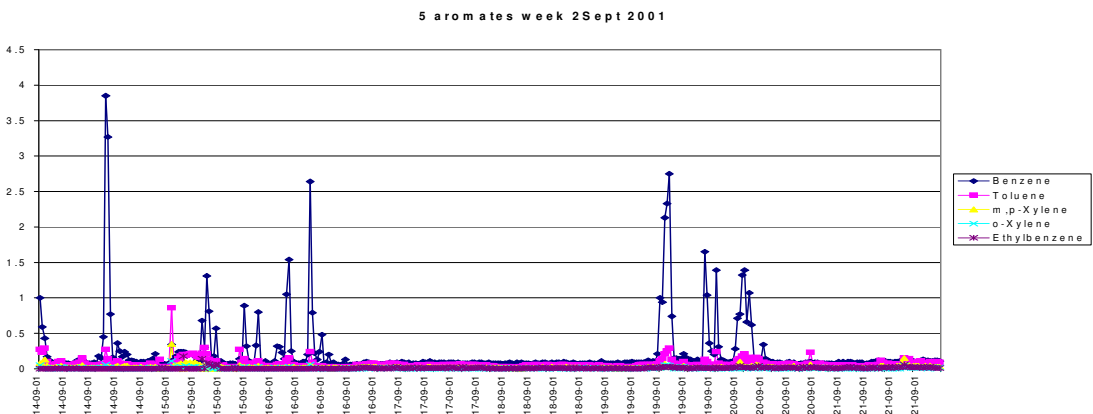
In the winter of 2000 and the autumn of 2001 a test was done near a refinery and a chemical industry in Norway. The industries conform to the local environmental regulations. The measurement point was west of the industrial zone. This meant that it was on the side of the nearest habitation, but with the most frequent wind situation the system was on the upwind side. Only during during some days in 2000 and one week in the period in 2001 was the station on the downwind side. Of these measurements some of the results are shown here. The batch-like nature of many chemical processes is clear: daily high emission of the C2-C4 hydrocarbons were measured at 14:00 during this whole week. For the more toxic hydrocarbons like benzene, chlorinated hydrocarbons and xylenes such a daily rhythm was not seen. Several high peaks were measured, clearly coming from different processes. The local background from traffic and household emission is very low. The mean values as measured were for all hydrocarbons below toxic levels.



Ethane emissions during one week at 14:00

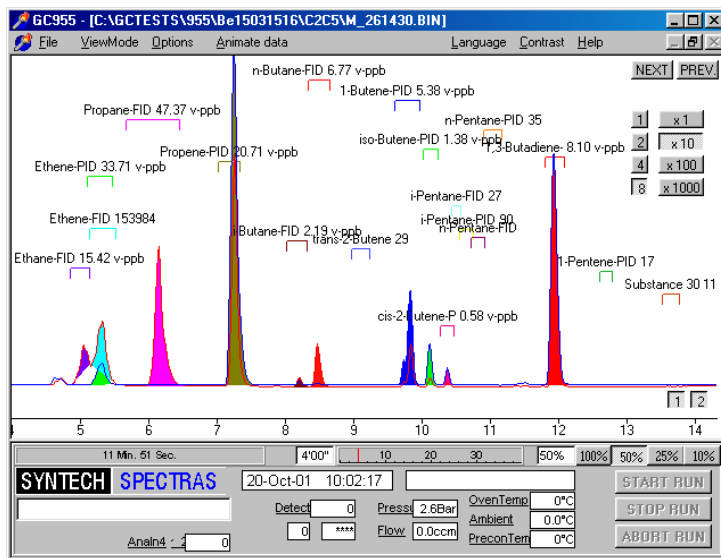


C4 hydrocarbons during one week, at irregular frequency

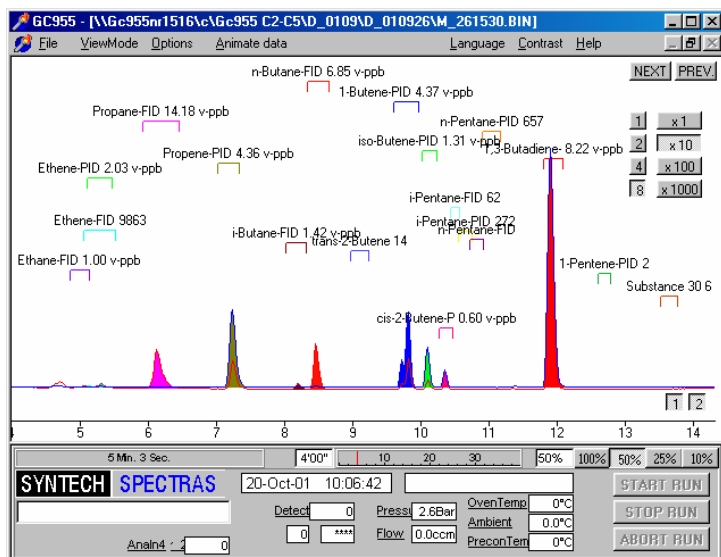


Aromatic components during one week

Chromatograms for the C2-C5 components

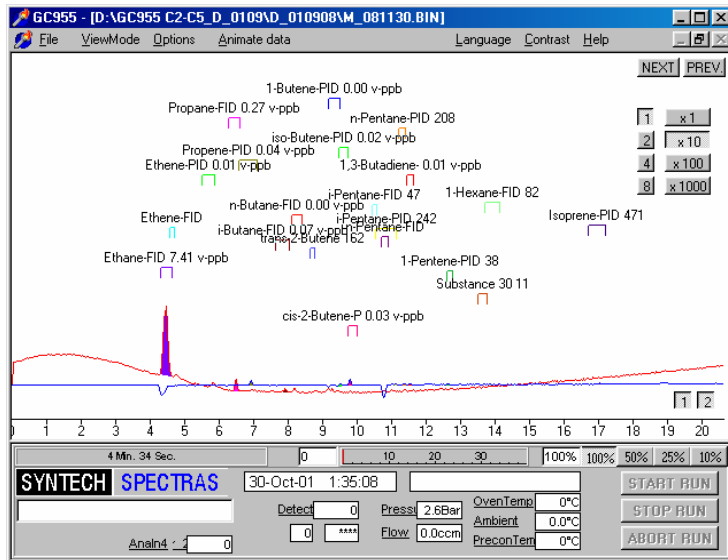


General high concentration for C2-C4



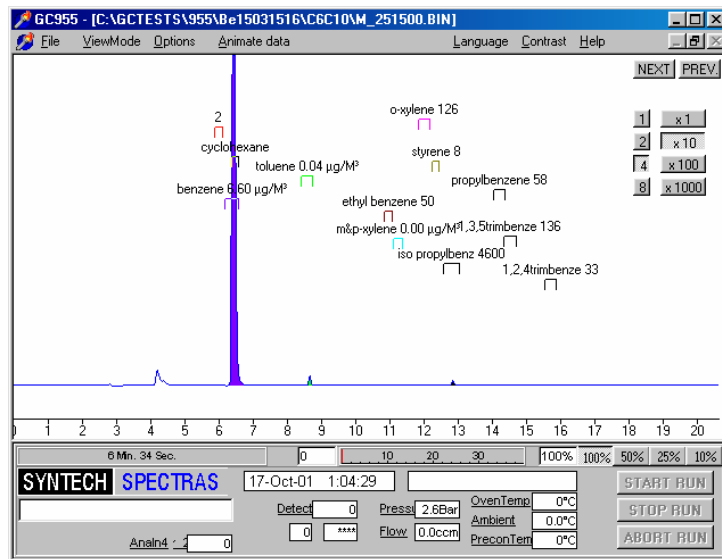
High concentration for C3-C4

The industry refines light hydrocarbons, mainly ethene, ethane, propene and propane. Of these propene is the most reactive ozone precursor. Due to the process, a high emission takes place at 14:00 every day. With the wind in the direction of the measurement station, this emission is measured. The local ambient air contains almost no C2 C4 hydrocarbons, so if no industrial emission takes place, the background chromatogram seems almost flat: the ethane measured is still from the industry.

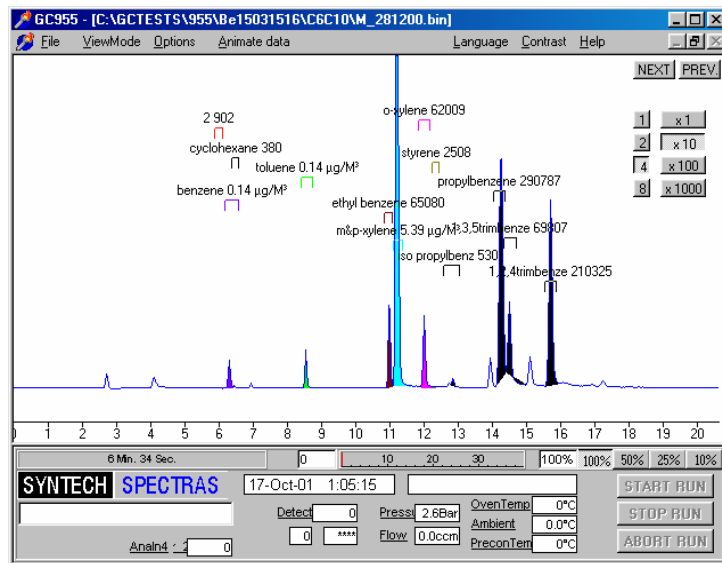


Local background chromatogram for C2-C5

Chromatograms for the C6-C10 components

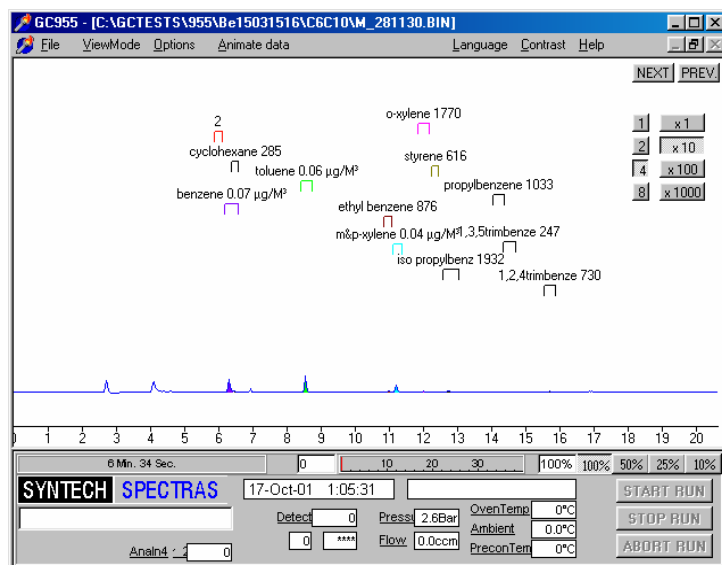


Singular benzene emission



Heightened concentrations for C8 and C9

In another sections of the refinery aromates are purified. The benzene is removed to fulfill the regulations for petrol. This may be the source for the singular benzene immissions. In several fractions of fuel, like kerosenes, benzene and toluene are almost absent, but the C8 and C9 aromates are present in higher concentrations. These immissions have high ozone formation potential. Also for the aromates, the background due to traffic is almost nil.



Local background chromatogram for C6-C10

Conclusion:

The ozone formation due to emissions of chemical plants and refineries is a major part of the ozone precursor problem. Even near a modern and well regulated plant high immmission peaks are seen daily that can only be contributed to the industrial emission. Depending on the source very regular or with changing frequency.

A time resolution of 30 minutes is the minimum to trap the short high peaks, shorter analysis times would be better.

The equipment as produced by Synspec can analyse the main components as emitted in Norway.