

The ratio of benzene and toluene in measurements of a background urban site at different weather conditions.

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Summary:

The hydrocarbons benzene and toluene have traffic as main source. Their fates can be quite different, depending not only on transport of the air, but also on light, temperature and humidity. The ratio of the cancerogenous benzene to toluene was studied during a 6 weeks period in the autumn at a background urban site.

This study had been set up to test a small automatic gaschromatograph for its suitability to measure in the field a range of hydrocarbons from C4 to C8. The instrument used works without consumption of liquid nitrogen or dry ice.

At the site studied, the toluene to benzene ratio varied by a factor 10. The "well-known" ratio in the range of 3 up to 5 was found at concentrations of > 1 ppb benzene. A very low ratio toluene to benzene of 1 to 2 was found at concentrations below 0.2 ppb benzene. In the cases where the ratio was this low, the butadiene concentration went down below 0.1 ppb, which was the detection limit of the equipment used. However with high ratios of 3 to 1 almost always 1,3-butadiene was detected.

The study shows clearly that at remote urban sites ratios of toluene to benzene are often below 1.

Keywords: Benzene, automatic monitoring

Les ratios de benzène et toluène dans les mesures de stations urbaines de fond avec différentes conditions météorologiques

Résumé:

Les hydrocarbures, le benzène et toluène proviennent essentiellement du trafic routier. Leur sort peut être différent non seulement selon la diffusion de l'air, mais aussi selon la lumière, la température et l'humidité. La proportion de benzène cancerogénique par rapport au toluène a été étudiée sur une période de 6 semaines, en automne sur un site urbain de fond.

Cette étude a été mise en place pour tester la capacité de mesure sur terrain d'un petit chromatographe gazeuse, automatique et compact, d'une gamme d'hydrocarbures allant de C4 à C8. Cet instrument fonctionne sans consommer ni azote liquide ni neige carbonique.

Sur le site étudié, le ratio de toluène sur benzène varie d'un facteur 10. Le ratio "bien connue" de 3 à 5 a été trouvée à des concentrations supérieures à 1 ppb de benzène. Un très faible ratio toluène/benzène a été trouvé pour des concentrations inférieures à 0.2 ppb de benzène.

L'étude montre clairement que dans les sites urbains éloignés les proportions de toluène par rapport au benzène sont souvent inférieures à 1.

Mots clés: Benzène, mesure automatique

Introduction

The hydrocarbons benzene and toluene have traffic as main source. Their fates can be quite different, depending not only on transport of the air, but also on light, temperature and humidity. (Council Directive 92/72/EEC 1992; Klemm et al, 1998). The health effects of benzene make their study important: it is cancerogenic. (Duffy and Nelson,1996 ; COM ,1998)

The ratio of benzene to toluene was studied during a 6 weeks period in the autumn at a background urban site. In this period photochemic activity in the air can be expected to be low, due to low temperatures and short daytimes. The period included several days with a stable high pressure situation, with inversion occurring during the night, in the first half of november. After this a period followed with several depressions passing the area. Due to the situation of the measurement site, on the south east of London, the concentrations resulting from the two weather situations can be expected to be very different: with an eastern wind and an inversion the concentrations rise steeply, to normal urban levels. With a depression and western winds the concentrations drop to low rural levels.

This study had been set up to test a small automatic gaschromatograph, the Syntech Spectras GC855, for its suitability to measure in the field a range of hydrocarbons from C4 to C8. The instrument used works without consumption of liquid nitrogen or dry ice, contrary to comparable instrumentation (Knoblauch et al, 1997; Oliver et al 1996) but uses a small cooler, modified from a laboratory bath to cool both a preconcentration and a gas chromaography oven. The detector is a PID.

Measurement results were compared to results from a Chrompack Voc-Air. These measurements were made by Dr. David Butterfield of the National Physical Laboratory in Teddington, UK.

1 Results

Measured concentrations

The measurements for benzene and toluene showed a very good agreement with the data from NPL. (fig. 1 , 2)

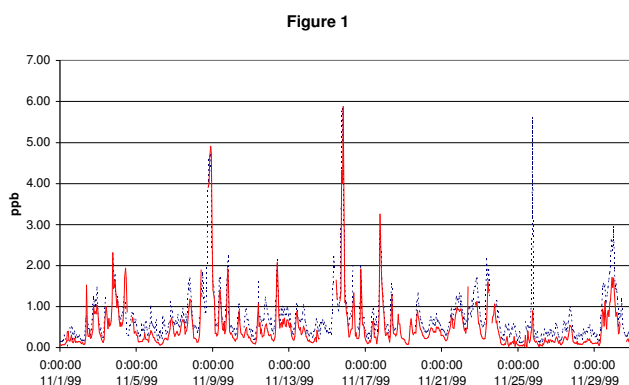


Figure 1, 2: Concentrations of Benzene (fig.1), Toluene (fig.2) measured from 1 to 30 November 1999 in Teddington (UK) with a Syntech Spectras GC855 (labelled Syntech Spectras: —) and a Chrompack Voc-Air (labelled NPL:). Values in ppb.

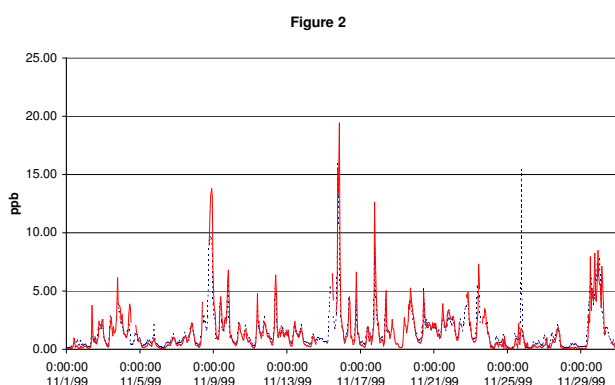


Figure 1, 2 and 3: Concentrations de benzène (fig.1) toluène (fig.2) mesuré de 1 à 30 Novembre à Teddington (UK)

2 Evaluation of the ratio of toluene to benzene

Ratios of toluene to benzene from the measurements at Teddington were often extremely low. The lowest values went to zero. Measurements with the same continuous GC, working at two city centres in the winter of 1999/2000 show that the rate is there much more stable and does not come below 1.5 in Italy and 2 in France.(fig. 4, 5 and 6).

In the air masses coming from the South West to the station at Teddington the toluene has already been oxidised. This despite the low temperatures and low ozone concentrations in November.

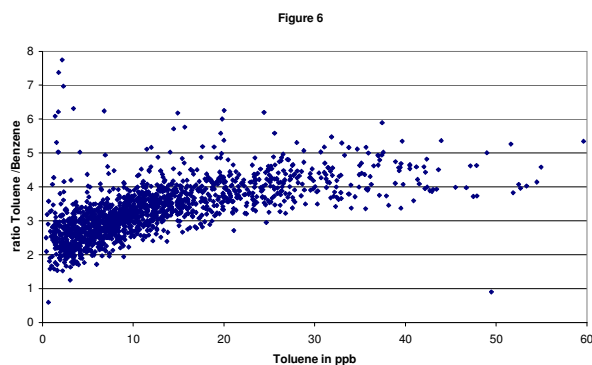
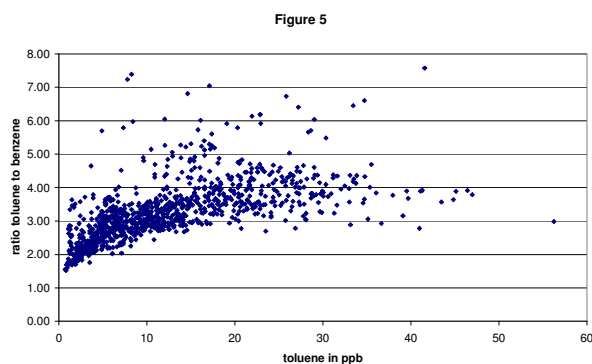
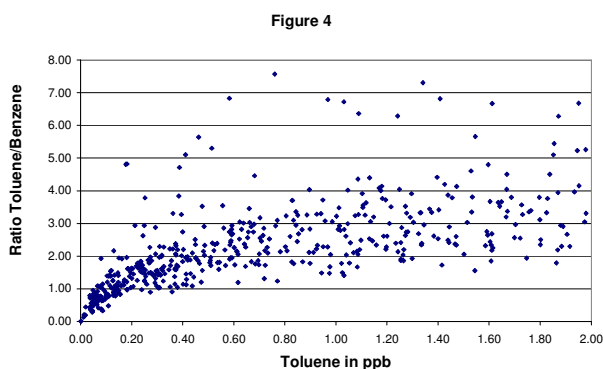


Figure 4, 5 and 6: Ratio of toluene to benzene against the toluene concentration at a remote city site near London (fig.4) and in a city centre in France (fig.5)and Italy (fig.6).

Ratio ppb to ppb. Scale for toluene in ppb.

Figure 4, 5 et 6: Ration de toluène à benzène dans un station urbaine de fond près de Londres et dans des stations urbaine central(fig. 4) en France (fig. 5)et en Italie (fig. 6).

Ration ppb à ppb. Echelle pour toluène en ppb

Chromatograms of measurements during inversion situations and during low pressure conditions

Such low ratios of toluene to benzene are not often reported. A possibility is of course a wrong identification of one of the 2 hydrocarbons. The chromatograms were evaluated with a view to this possibility. After evaluation it seems unlikely that a wrong identification is the cause of the unusual ratio. The retention times are stable for benzene and toluene. Especially with the very low concentrations no possible interfering peaks are found near benzene and toluene.

In the measurement period some days with inversion occurred. This resulted in a sharp rise in the concentration of benzene and toluene, and also 1,3-butadiene was then present. (Figure 7) The ratio of toluene to benzene is very clearly in the normal range when this occurs. However normally the weather in the low regions of Northern Europe does not lead to inversions. As these situations are the exception, the situation with a low ratio of toluene to benzene is more interesting. (Figure 8) In these situations not only the benzene and toluene concentrations are low, also all other hydrocarbons have very small peak areas.

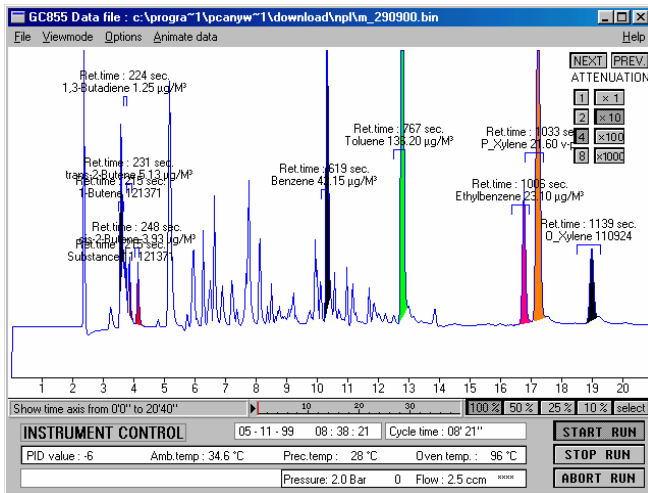


Figure 7: High concentrations and ratio 3 of toluene to benzene in an inversion situation
Figure 7: Hautes concentrations et un ration de 3 de toluène à benzène

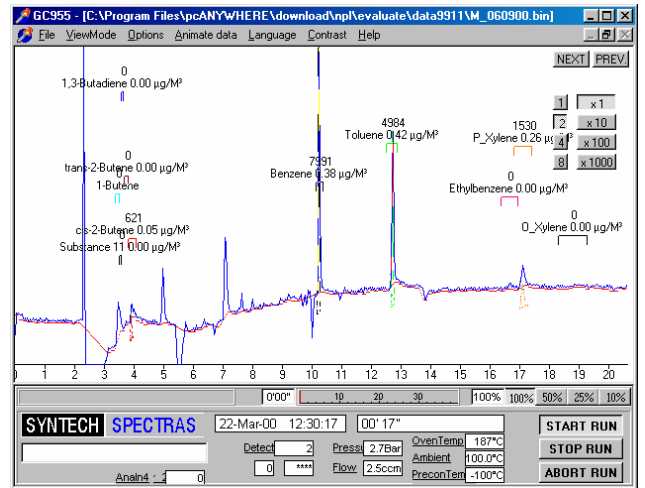


Figure 8: Low concentrations and ratio 1 of toluene to benzene in a depression situation
Figure 8: Basses concentrations et un ration de 1 de toluène à benzène

Conclusions:

1. At remote sites, even if they are a city background in winter, toluene to benzene ratios are often below the standard well-known values ranging from 3 to 5.
2. With these low ratios of toluene to benzene, also low 1,3-butadiene concentrations occur.

Acknowledgements:

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