# FINGERPRINTING BAYER REFINERY AIR EMISSIONS USING $\delta^{13}$C COMPOSITIONS OF SELECTED VOCS BY COMPOUND SPECIFIC ISOTOPE ANALYSIS (CSIA)

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## Abstract

Determining the contribution of alumina Bayer refining to VOCs in ambient air is complex mainly due to the fact that many of the organic compounds are ubiquitous. Organic molecules from different sources have been differentiated in solid and liquid samples using the stable carbon isotope compositions ($\delta^{13}$C). This has been particularly useful for petroleum samples when traditional petroleum biomarkers have been unsuccessful at determining the source of hydrocarbons.

The current work describes the use of a novel method to measure the $\delta^{13}$C compositions of VOCs in an alumina refinery stack and a car exhaust gas sample for the first time. The method involves using a sorbent tube trap and then analysing by direct thermal desorption/CSIA. The $\delta^{13}$C values of several VOCs in an Alcoa World Alumina refinery calciner stack and a car exhaust air samples were measured and showed that the $\delta^{13}$C of several common organic compounds (e.g. benzene and toluene) in the two sample types were similar. Interestingly the isotopic ratios of other compounds (e.g. Ethylhexanol) in the refinery stack were significantly different to the other VOCs and may be a useful marker.

## 1   Introduction

The atmosphere contains a complex mixture of organic compounds, as either volatiles or aerosol particulates. These organic compounds derive from a variety of natural materials (e.g. wind blown plant waxes, vegetation and soils) or from anthropogenic emissions (e.g. vehicle exhaust and industrial effluents/soot). Determining the contribution from these sources to ubiquitous ambient VOC, such as benzene, is difficult. One approach to deconvoluting this is to use a method that can differentiate the same molecule at the isotopic level such as TD-GC-ir-MS.

## 2   Experimental

*Sampling and Analysis by GC-ir-MS*

Stack sampling was carried out on an alumina calciner stack. A glass adsorption probe was inserted 345 mm into the sealed sampling port on the stack and as the stack has approximately 100 mm lagging the effective distant of the glass probe into the stack was 200 to 250 mm.

Vehicle exhaust sampling was performed on a 1994 family model sedan running on unleaded petrol. Prior to each sample the vehicle was idled for 10 minutes to reach operating temperature. The glass probe was inserted 220 to 230 mm into the exhaust pipe with the aim of having the end of the probe in the centre of the pipe.

Gas Chromatography – Isotope Ratio Mass Spectrometry (GC-ir-MS) analyses were carried out on the samples using the method published elsewhere (Turner et al. 2005).

## 3   Results and Discussion

**3.1** *Analysis of VOCs in industrial emission and car exhaust by TD-GC-irMS*

The identification of VOCs was based on TD-GC-MS peak retention time matching those of authentic standards. Isotopic signatures for VOCs in a calciner stack sample were obtained and span the range from –23.5‰, for benzene, to –31.5‰, for 2-Ethylhaxanol (Figure 1; Table 1).

Studies examining stable isotopes at or near natural abundance levels are usually reported as delta, a value given in parts per thousand or per mil ('o/oo'). Delta values are not absolute isotope abundances but differences between sample readings and one or another of the widely used natural abundance standards which are considered to have deltas of zero. For carbon isotopes, the standard is Pee Dee Belemnite, At%13C = 1.1112328. Absolute isotope ratios (R) are measured for sample and standard, and the relative measure delta is calculated:

R= (Atom%13C)/(Atom%12C)
D13C (std) = ((R sample- R std)/ R std) x 1000 in per mil

So the value of –23.5 per mil for benzene means that benzene in the calciner gas contains more 12C relative to the standard and is negative. 13C/13C ratio R is less than the standard's R by 23.5 parts per thousand, this value is reported as delta 13C = –23.5 delta o/oo.

VOC identifications were based on TD-GC-MS peak retention time matching those of authentic standards. Isotopic signatures for 12 compounds in the car exhaust emissions were found to span a tight range from –22.8‰ to –26.3‰. The major components benzene and toluene had $\delta$13C of –24.0 ± 0.17‰ and –24.5 ± 0.18‰ respectively (Table 2).

**3.2** *Comparison of the Stack and Car Exhaust Samples*

Comparison of the isotope signatures of the benzene and toluene in both the stack and car exhaust samples shows that a negligible difference exists between the compounds from the two sources. The error of the analysis for the stack samples and car exhaust samples was within 0.65‰ and 0.20‰ respectively. The precision of the instrument is ± 0.2‰. Therefore a difference of <1‰ is negligible and would be particularly difficult to track in the environment.

Table1. Isotopic signatures (δ13C ‰ relative to VDPB) and standard errors of VOCs in calciner stack emissions.

| Compound | $\delta^{13}C$ (‰) | Standard Error |
|---|---|---|
| MEK* | −23.9 | 0.65 |
| Benzene | −23.5 | 0.11 |
| Toluene | −25.4 | 0.48 |
| 2-pentene** | −28.0 | 0.34 |
| 2-ethylhexanol | −31.5 | 0.12 |

* – co-elution of peak, at front and back, ** – partial co-elution

Most interestingly, the 2-ethylhexanol in the calciner stack is much more depleted in 13C than the other compounds, with a value of −31.5‰, and this is possibly because it originates from a dewatering aid used in the hydrate pan filters.

Table 2. Isotopic signatures (δ13C ‰ relative to VDPB) and standard errors obtained for 12 compounds from the car exhaust emission samples.

| Compound | $\delta^{13}C$ (‰) | Standard Error | Compound | $\delta^{13}C$ (‰) | Standard Error |
|---|---|---|---|---|---|
| A | −25.3 | 0.19 | G | −23.3 | 0.08 |
| B | −23.2 | 0.10 | H (Benzene) | −24.0 | 0.17 |
| C | −24.4 | 0.03 | I (Toluene) | −24.5 | 0.18 |
| D | −23.8 | 0.08 | J | −26.3 | 0.06 |
| E | −24.0 | 0.08 | K | −25.1 | 0.15 |
| F | −22.8 | 0.05 | L | −25.6 | 0.14 |

## 4    Conclusions

A robust, previously published, method was developed and used for the TD-GC-irMS analysis of an alumina calciner stack and a car exhaust. Although some key VOCs such as benzene and toluene had similar $\delta^{13}C$ values, others such as Ethylhexanol were very different and may be useful as an environmental maker for the calcination area of an alumina refinery.
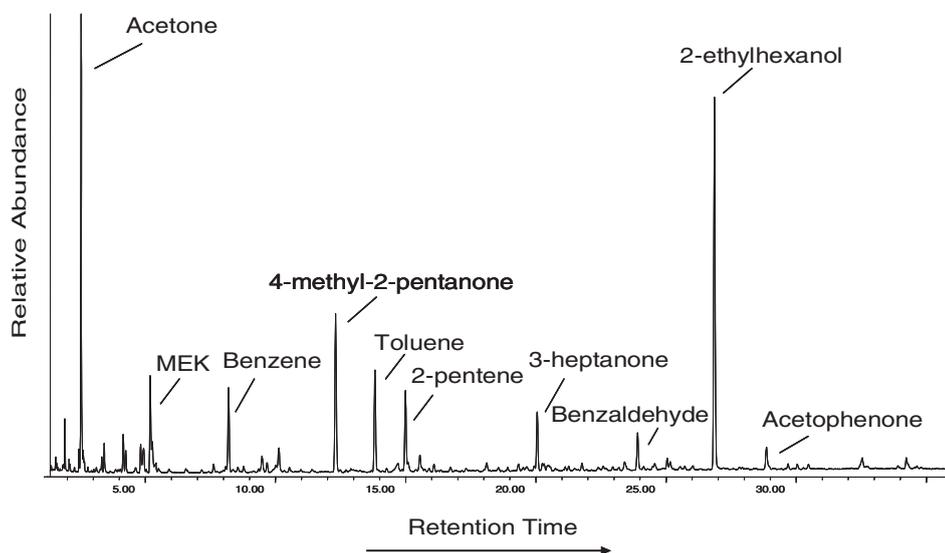


Figure 1. GC-MS (TIC) trace of calciner stack emissions, with all the major peaks identified.

## References

**Turner N., Jones M., Grice K., Dawson D., Ioppolo-Armanios M. and Fisher S.** (2005) 13C of Volatile Organic Compounds (VOCs) in Airborne Samples by Thermal Desorption-Gas Chromatography-Isotope-Ratio-Mass Spectrometry (TD-GC-irMS). Environmental Science and Technology, submitted.