# Real-time Quantification of Impurities in Food-Grade $CO_2$ with PTR-MS

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## Introduction

Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) is a well-established technology for **real-time analysis** of volatile organic compounds (VOCs), which is characterized by high sensitivity, low Limit-of-Detection (LoD), short response time and direct injection without any sample preparation.

Typical applications can be found in various fields such as **environmental sciences, food and flavor** research and many more [1].

In recent years analytical challenges in trace gas detection have become more and more demanding and the need for instrumental performance has continuously grown.

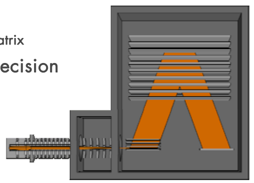
A powerful option to meet these requirements is the **optimization** of the **ion transfer system** between the PTR ionization region and the TOF mass spectrometer, which can **increase the overall sensitivity by orders of magnitude**.

Here we introduce an new instrument, the **PTR-TOF 1000 ultra**, which is a compact PTR-TOFMS equipped with an **ion funnel**. Its high sensitivity makes the PTR-TOF 1000 ultra a perfect tool for applications where complex matrices have to be **rapidly analyzed** for example in quality assurance in the food and flavor industry.

One such application is the real-time quantification of **impurities in food-grade carbon dioxide** (CO2), which we present here as a practical example.

## Proton-Transfer-Reaction (PTR)

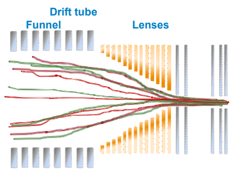
- "Soft" ionization of VOCs
  - low fragmentation
  - important in complex matrix
- Accuracy < 5 %, precision < 2 %
- Real-time < 100 ms
- High sensitivity, LOD < 1 ppt



$$H_3O^+ + VOC \longrightarrow VOC.H^+ + H_2O$$

## Novel ION BOOSTER

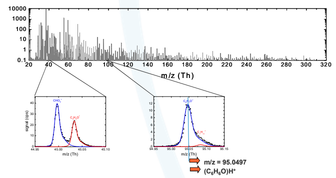
- Improved ion transfer
  - up to x10 more sensitivity
  - Ion-funnel between PTR ionization and TOF
- Upgrade of existing PTR-MS
  - Modular design
- Perfect integration
  - PTR, funnel, TOF, all manufactured in-house




The ion-funnel, consisting of a series of lenses with decreasing apertures and applied RF voltages, focusses the ion trajectories.

## Time-of-Flight (TOF)

- Full spectrum in a split-second




- High mass resolution
  - Separation of isobars
  - Identification of chemical composition

- Lower LOD (< 5 ppt)

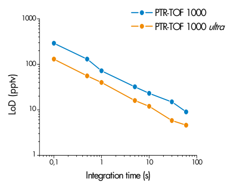



**Figure 1**: **LoDs** at m/z 147 for **PTR-TOF 1000** and **PTR-TOF 1000 *ultra*** for integration times between 0.1 and 60s. LoDs are calculated using the 3σ (standard deviation) method.

- Higher sensitivity across entire mass scale

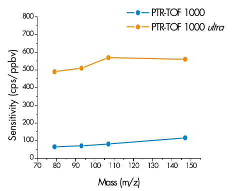



**Figure 2**: Comparison of the **sensitivities** for **PTR-TOF 1000** and **PTR-TOF 1000 *ultra*.** The sensitivities are obtained utilizing compounds from certified gas standards.

- Better S/N, faster measurement

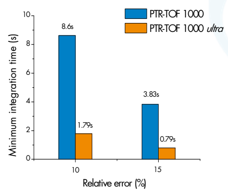



**Figure 3**: Considerably less integration time (s) needed to achieve a relative error of **10% (15%)** for **PTR-TOF 1000 *ultra*** than for **PTR-TOF 1000**, while analyzing a concentration of 100 pptv.

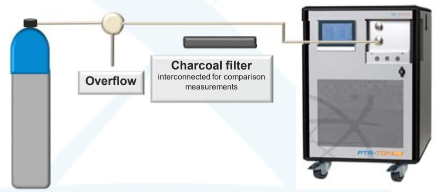
- Compact dimensions

## Impurities in Food-grade $CO_2$

The modern food and beverage industry is not imaginable without food-grade carbon dioxide. Its many uses include carbonation of beverages, and as packaging and cooling gas. Therefore, we investigated **volatile organic impurities** emerging from a **food-grade** certified (European standard E 290) **carbon dioxide cylinder** with a PTR-TOFMS instrument.

In a first step we compared the high-resolution mass-spectra from the analysis of the $CO_2$ cylinder a) unfiltered and b) filtered by a charcoal filter (see experimental setup, **left**). The filtered gas serves as a reference for the background of a VOC-free $CO_2$ matrix. **Figure 4** illustrates that most compounds are suppressed during filtration and therefore constitute **organic impurities, most with mass-to-charge ratios higher than m/z 150 and concentrations in the range of 100 pptv to 10 ppbv.**

In a next step we monitored the concentrations of several main impurities over time (**figure 5**). Immediately after opening the cylinder.



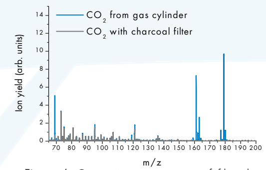




**Figure 4:** Comparing mass spectra of filtered (=background) and unfiltered $CO_2$. Several **impurities in food-grade $CO_2$** are visible.

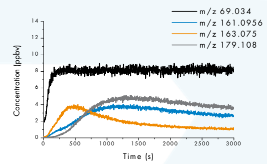



**Figure 5**: **Concentration vs. time**. Impurities show different dynamic, which is attributed to their vapor pressure in the cylinder.

We observed that only one compound (m/z 69.034) reached a constant concentration. Other **compounds showed a dynamic behavior**, with maxima at different times. We attribute this behavior to the outgassing head-space concentration inside the gas cylinder, which depends on the **individual vapor pressure and outgassing dynamics** from the liquid $CO_2$.

Consequently, the **time** between opening the $CO_2$ **cylinder** and introduction of the gas into food can have an **influence on the level of impurities** measure in the QA as well as in the final product.

These results emphasizes the **great advantage of real-time analysis in food & flavor quality assurance.**

**References** [1] A.M. Ellis, C.A. Mayhew, In: Proton Transfer Reaction Mass Spectrometry: Principles and Applications, Chichester, UK: John Wiley & Sons, Ltd (2014).

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