

Long-term monitoring for trace gases by using

Introduction

In the field of gas monitoring, the concentration of multiple species of gas components must be continuously and stably monitored in real time at intervals on the order of a few seconds. Moreover, if any unexpected impurities are detected during the monitoring interval, these must be identified with a high degree of certainty. Real-time monitoring of the concentration of multiple gas components at fewsecond intervals is difficult with typical GC or GC-MS measurement systems. In some cases, gaseous emissions have been injected directly into a quadrupole mass spectrometer (QMS) for measurements at few-second intervals; however, if any unexpected impurities are present during this process, the limited mass resolution and mass accuracy of QMS measurements make it difficult to reliably identify them.

In this application note, we report the use of MSI Tokyo's infiTOF system for real-time, stable, continuous monitoring of multiple gas components at few-second intervals, with sufficient mass resolution and mass accuracy to allow identification of unexpected impurities.



infiTOF

Experimental conditions

Standard gases (10 ppm each of CH₄, N₂, CO, O₂, Ar, Kr, and Xe in a He base) were connected to the inlet of a massflow controller. The infiTOF ion source was connected directly to the outlet of the mass-flow controller, and the flow rate was set to 2 cc/min. The infiTOF was set to highresolution mode (40 cycles) and the intensity of a total of 8 gas components including the 7 standard gases listed above plus H₂O was continuously monitored at 1-second intervals for 10 hours. (Detailed experimental conditions are listed in Table 1.)

Table. 1 Experimental conditions for long-time

Item	Description
Instrument	infiTOF
Gases used	CH ₄ , N ₂ , CO, O ₂ , Ar, Kr, Xe (10 ppm each in He base)
Carrier gas flow rate	2 [cc/min]
El ionization energy	20 [eV]
infiTOF cycles	40 cycles

When making measurements continuously over long time intervals, the intensity and position of peaks in mass spectra are affected by temperature variations in the vicinity of the instrument. In this measurement, we monitored the peak intensities and positions as the experiment proceeded, using Ar ions as reference ions. We used the results of these measurements to correct the spectra of the other gas components.

Results and Discussion

Figure 1 shows mass spectra for CH₄, H₂O, N₂, CO, O₂, Ar, Kr, and Xe as measured by the infiTOF in highresolution mode. Figures 2(a-g) are enlarged views of the peaks in Figure 1.

Note that, in this measurement, we did not use a column or other means to separate CO from N₂. Instead, the mass resolution of the infiTOF alone suffices to achieve the complete separation of peaks all the way out to the tails of the peaks like those in Figure 2(c). In high-resolution mode, we achieved a resolution on the order of 10,000.

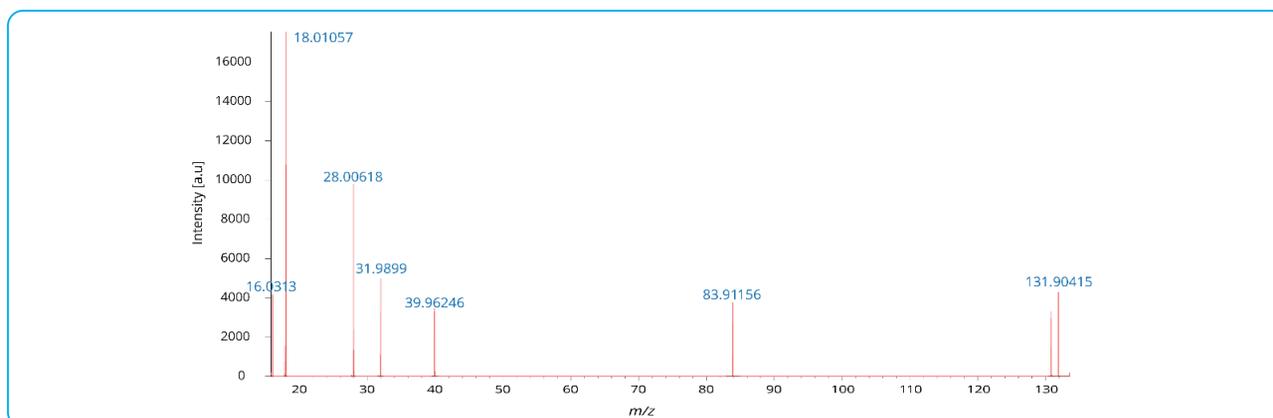


Fig. 1 Mass spectra of CH₄, H₂O, N₂, CO, O₂, Ar, Kr, Xe

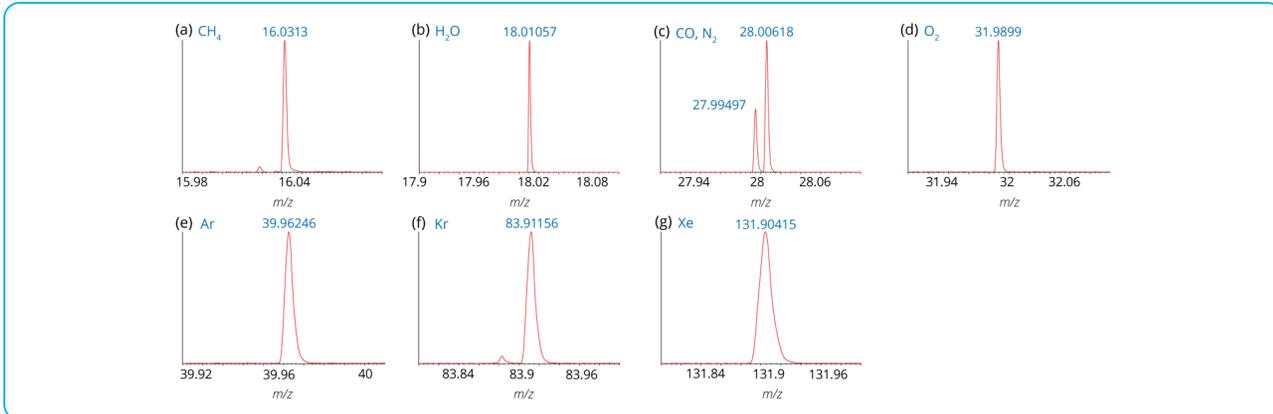


Fig. 2 Mass spectra of CH₄, H₂O, N₂, CO, O₂, Ar, Kr, Xe (enlarged near peak regions)

Table 2 shows the results of calibrations applied to the mass spectra in Figure 1 with CH₄ and Xe used as calibrants; the table lists the theoretically predicted values, the values computed from the measured data, and the difference between the two. For all components, the mass value we obtained differs from the theoretical value by 5 ppm or less, demonstrating that this measurement technique offers sufficient mass accuracy to reliably measure the target components.

Table. 2 Calibration results

Targets	Theoretical value	Experimental value	Error [u]	Error [ppm]
CH ₄	16.03130	Calibrant	-	-
H ₂ O	18.01057	18.01057	0	0.0
CO	27.99492	27.99497	0.00005	1.8
N ₂	28.00615	28.00618	0.00003	1.1
O ₂	31.98984	31.98990	0.00006	1.9
Ar	39.96238	39.96246	0.00008	2.0
Kr	83.91151	83.91156	0.00005	0.6
Xe	131.90415	Calibrant	-	-

Figure 3 shows chromatograms for the gas components targeted by the measurements. (Values on the vertical axis are normalized by the intensity of Ar.) With the exception of H₂O, none of the standard gas components targeted by the measurements exhibited marked variation during the course of a 10 hour continuous measurement. Indeed, the change in relative intensity never exceeded 1% per hour.

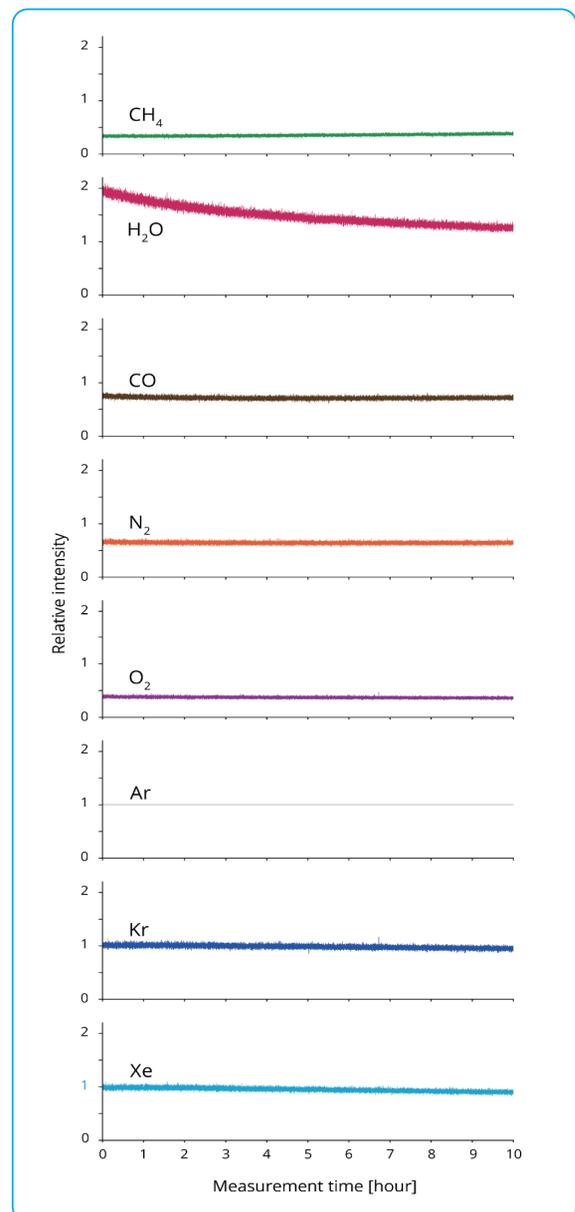


Fig. 3 Mass chromatogram of CH₄, H₂O, N₂, CO, O₂, Ar, Kr, Xe

The figure shows that the H₂O concentration exhibited a slight variation. Because H₂O was not inserted into the ion source as a sample, this indicates that the experiment was monitoring residual quantities of H₂O present in the vacuum chamber or the guiding pipes. These results indicate that the residual H₂O concentration gradually decreased over the duration of the measurement.

Thus, the high-resolution mode of the infiTOF allows complete separation of peaks corresponding to separate components. Using reference ions, it is possible to achieve stable continuous monitoring of peak intensities and positions for multiple gas components.

Conclusion

Using the infiTOF system, we conducted an experiment involving 10-hour continuous monitoring of 8 species of gas components at 1-second intervals in real time. We obtained mass spectra with a resolution on the order of 10,000 and a mass accuracy within 5 ppm. The relative intensity variation for each chromatogram never exceeded 1% per hour, indicating successful achievement of stable long term continuous monitoring.

The infiTOF system allows stable, continuous real time monitoring of intensity variations in multiple target gas components while retaining sufficient mass resolution and mass accuracy to allow identification of unexpected impurities. This shows that the infiTOF can play a valuable role in the field of gas monitoring.

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