The Claviature of Gas Analysis

Mass spectrometric gas analysis for quality assurance of gases and gas mixtures

High purity and special gases are becoming increasingly important in the development of modern technologies. The demand placed on purity and diversity of mixture formulations are constantly challenging manufacturers and users in production, quality control and the use of these gases and gas mixtures. The required analytics is becoming increasingly complex and can only be realized by applying and combining a wide variety of methods. Using the example of analytics in a dedicated gas center, examples of tasks and solutions are outlined.

By VOLKER FREY, MICHAEL BRUDEL

Dr. VOLKER FREY is Deputy Head of the Special Gases Centre of the Westfalen AG in Hörstel, Germany

Dr. MICHAEL BRUDEL is responsible for product support and marketing at InProcess Instruments in Bremen, Germany.

Various techniques and processes are used for the production and quality assurance of gases and gas mixtures. A flexible and efficient analysis technology is particularly needed for customer-specific gas mixtures. Mass spectrometry (MS) is a valuable addition to standard techniques (GC, IR, UV, etc.) and to a variety of special methods. It is ideally suited to a variety of problems.

Westfalen's Special Gases Center, a manufacturer of technical gases founded in Münster in 1923 and now active throughout Germany, focused primarily on maximum flexibility of the mass spectrometer for a wide range of measurement tasks when it purchased the Instrument.

Westfalen's Special Gases Center uses various analytical systems to quantify customer-specific gas mixtures.

The special version of a GAM 400 from InProcess Instruments, which has three gas inlets connected to a quadrupole mass analyzer, came closest to this requirement. Based on joint preliminary tests and intensive discussions, the system was designed and tailor-made for Westfalen.

The strengths of the individual analysis methods and in which cases the combination of several methods is necessary, is exemplified by various application examples, which can be assigned to the fields of activity in the Specialty Gases Centre Hörstel:

- High purity gas analysis;
- Analytics for the exact characterization of customer-specific gas mixtures;
- Development of analytical methods for new components in gas mixture formulations and
- Analysis orders.

For each of these areas, specific methods and analysis strategies are in place.

Analysis of high purity gases

For this application, the produced high purity gases (nitrogen, argon, oxygen, hydrogen, helium, carbon dioxide) are tested for secondary components (impurities) as part of the routine analysis. Depending on the constituents, the high-purity gases are produced up to 6.0 gas purity (corresponding to 99.9999 percent purity). This implies that the total of the secondary constituents must not exceed 0.0001 vol. percent = 1 vol. ppm. The analytical instrumentation is optimized such that it reliably measures the corresponding secondary constituents within the specified concentration range in a wide variety of gases.

Gas chromatography with helium or argon ionization detectors is used for the most part. The advantage of these detectors is the low detection limit (vol. ppb range) of the permanent gases e.g. in the air. The disadvantage results with only two decades from the low range of linearity. Various instruments are used to determine the moisture content in gases. They can be based on dew point mirrors, phosphorus pentoxide, capacitive aluminium oxide measuring cells or oscillating quartz technology. Traces of Oxygen are detected up to the volume ppm range using the redox measurement method.

In order to carry out these these measurements, precise calibration gases are needed that have to be produced and tested. The quality assurance of these test gases is done by mass spectrometry. The advantage of this method particularly results with more than six decades from the very large linearity range. On the other hand, the zero point of the component in question has to be determined as accurately as possible. The use of gases with quality 6.0 is not sufficient. Therefore, highly efficient post-cleaning processes are deployed.

Analytics of customized gas mixtures

The GAM 400 mass spectrometer, here with different inlet systems, serves a mass range of 1 to 300 amu.

In this field of work, gas mixtures, which are produced according to the customer's wishes and recipe, are analyzed for their true value. The prerequisite for production of such customized gases is, among other things, a official manufacturing permit and the infrastructure for testing or ensuring the stability of the gas mixtures. Hence, all potential chemical reactions between the individual components and the gas cylinder and the valve material must be examined.

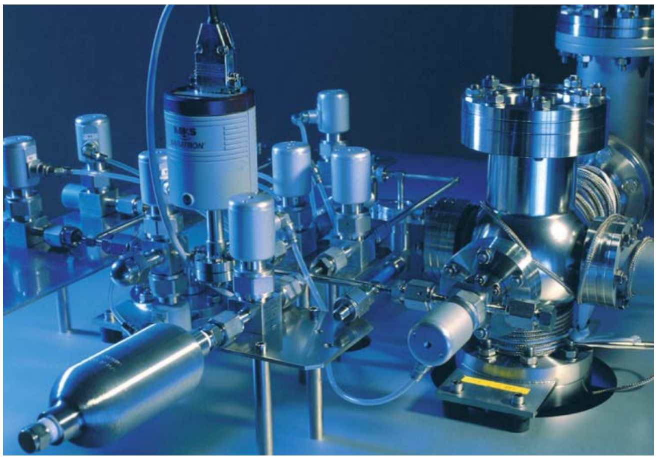
Westfalen's Specialty Gases Centre currently stocks approx. 150 individual components, which are gravimetrically combined to customer-specific formulations depending on feasibility. To date, these formulations contain up to 20 individual substances. The concentrations that can be produced and analyzed range depending on the substance from a few vol. ppb to the percentage range. New recipes are added almost daily to the approx. 4,000 recipes already stored.

The combination of different analytical methods is often used to effectively achieve correct results. Beside the classical gas chromatography with different separation columns and detectors (WLD, FID, FPD, ECD), mass spectrometry, infrared spectroscopy (NDIR, FTIR) and the chemiluminescence method (partly parallel) are also used - depending on the analytical question.

With over 4,000 different recipes, it is difficult to assess, which techniques should be used and when. In general, the measuring procedure must be unambiguous. For example, in mass spectrometry or IR spectroscopy masses or wave numbers that are interfered by other components of the mixture must not be used. With GCs, it is important that the evaluated components do not have the same retention times. Cross-sensitivity, artifact formation and quenching effects must be considered. Hence, method development and validation take up a considerable part of the time for the entire analyses. Standardized analytical methods are used for frequently analyzed formulations.

Analysis of new components in gas mixtures

New or additional components specified by the users have to be mixed into existing gas formulations. This determines the further procedure. Before actual production, test and release procedures have to be followed for the new components, which go beyond those described in the previous section. Only then, reference gases are independently of one another produced in accordance with EN 6142. The methods suitable for quantitative measurement are then tested in compliance with DIN EN 6143. All analytical equipment and methods present in the Specialty Gases Centre are considered. Where possible, these gas mixtures are also validated with external standards. Finally, the new formulations are tested for stability.



Mass spectrometer systems are highly selective and capable of multi-component analysis.

Contract analytics

In Special Gases Centers as described above, most known gas mixtures are analyzed quantitatively only. Unknown gas mixtures are measured both, qualitatively and quantitatively after the analytical method has been developed. After a qualitative analysis with FTIR and MS (spectra recording in scan mode), next steps for the systematic procedure is determined case-by-case.

Combination of different analytical methods

One example is the production of 500 vol. ppb of sulfur isotope 34 (34SO2) in sulfur dioxide in nitrogen. Due to the low concentration of the 34SO2 in the mixture, the mass spectrometer is here not suited for the quantitative analysis. Therefore, the quantitative analysis is performed with a sulfur dioxide analyzer. This UV spectrometer has a detection range from 0.1 vol. ppb to 500 vol. ppb. However, only the mass spectrometer can be used to test the isotope distribution in pure sulfur dioxide.

Traces of nitrogen monoxide, sulfur dioxide and carbon monoxide mixed with nitrogen as main component are particularly difficult to analyze. Th gas chromatography at the Special Gas Centre is not sufficient for such mixtures. This is why nitrogen monoxide is analyzed with the chemiluminescence analyzer, while sulfur dioxide and carbon monoxide are quantified with the IR spectroscopy.

Application of the mass spectrometer

Depending on the method, the mass spectrometer system can be used for a wide range of analyses in the Specialty Gases Center. It is therefore one of the most important and versatile analytical instruments. This is because of the universality of the measurement principle, which is characterized by high selectivity, multi-component capability, short measuring times, high sensitivity and a wide dynamic range.

The verification of the accuracy of analytical results by the analysts is of great importance.

The MS is used as for special analysis methods of high purity gases, gas mixtures and special gases. Besides the direct quantitative determination of trace components down to the ppm range, it is also possible to measure isotopic compositions. The technique is particularly strong in the determination of non-polar molecules, such as noble gases. The instrument has been specially designed for fast and accurate gas analysis of the mass range 1 to 300 amu. The combination of different gas inlets makes it particularly well suited for the special gas center because it has…

- a batch inlet for the measurement of smallest gas quantities ;
- a direct capillary inlet for highly reactive components such as chlorine a gas inlet for routine analyses with a continuous gas flow
- a possibility to switch to a second gas flow, e.g. for calibration or zero gas measurements.

The flexible solutions of the instrument technology as InProcess Instruments develops and manufactures them, enable a wide use of mass spectrometry for many different tasks. It is therefore a valuable addition to other analytical methods at the Westfalen's Specialty Gases Center. Like IR spectroscopy (not all gases are IR-active or have only weak absorption bands), mass spectrometry also has its limits because of its physical principles. The formation of artifact ions in the ion source by gas phase or wall reactions must be considered for certain gas compositions. For example, the exact quantitative determination of a few vol. ppm nitrogen monoxide in mixtures containing nitrogen and oxygen is very difficult. Surface effects in the vacuum region of the mass spectrometer must be particularly taken into account when interpreting the measurement results of trace components. For example, the mass spectrometer is not the method of choice for the determination of traces of water in gas mixtures.

For quadrupole analyzers with limited mass resolution, certain restrictions also apply to the quantitative acquisition of components with mass interferences. For example, the exact determination of carbon monoxide (mass number 28) in nitrogen (also mass number 28) by a matrix calculation of the fragments is only possible in the percentage range.

A wide range of measurement methods and instruments are necessary for demanding gas analysis. Yet mass spectrometry plays an outstanding role. In addition to high-resolution sector field mass spectrometry and the many special systems for bio- and elemental analysis, quadrupole mass spectrometers are of particular importance for gas analysis because of their flexibility and good price/performance ratio. For the full benefit of this technology, an individual instrument concept and application-related guidance and support are required before and after the purchase of the instrument.

Conclusion

Quality assurance of ultrapure and special gases is becoming increasingly complex and requires new, sophisticated solutions. Adding a mass spectrometer to the analytical toolset provides new possibilities for gas analysis and quality control. The GAM 400 from InProcess Instruments is a device used in Westfalen's Special Gases Centre for a wide range of measurement tasks, such as isotope purity control, the quantitative detection of non-infrared sensitive compounds and the determination of gas concentrations in mixtures. This quadrupole mass spectrometer specifically designed for the tasks at Westfalen is best suited for fast and precise gas analysis at a mass range of 1 to 300 amu. Several gas inlets allow trace measurements of reactive components as well as high precision measurements with low sample consumption.

Quoted from Web Magazine P&A, June 2005