Analysis of Ethanol in Fermentation Process Offgas

Applications in Pharmaceutical and Bioethanol Production

Introduction

AMETEK's ProLine and ProMaxion Process Mass Spectrometers have been used successfully for many years in fermentation process control, monitoring both aerobic and anaerobic processes.

As well as monitoring the standard air gases (nitrogen, oxygen, argon and carbon dioxide), the MS is able to monitor other volatile species in the offgas. There has recently been a dramatic interest in monitoring ethanol in the offgas at ppm levels. This interest has come both from the pharmaceutical industry and from the rapidly expanding interest in biofuels such as bioethanol.

This application note describes the ability of the AMETEK system to measure ppm levels of ethanol accurately and precisely in the presence of percentage levels of oxygen.

The Applications

Ethanol can be produced as a product or by-product of fermentation. In the pharmaceutical industry, its presence can be an early indication of a fermentation process going off-specification so there is a requirement to monitor it alongside the standard air gases.

Recent interest in replacement fuel technologies has seen the development of a number of processes to develop bioethanol, from traditional processes turning corn into starch then fermenting it to ethanol, to processes based on fermentation of non-food based, low value starting materials such as agricultural waste, straw waste etc.

In all these processes, there is the requirement to measure ppm levels of ethanol in the presence of percentage levels of oxygen. While mass spectrometers in general offer multi-component analysis, this analysis requires a MS with a high level of analytical performance if it is to be carried out reliably.

The Analysis

Ethanol (C_2H_6O) has a molecular weight of 46. In the electron impact ion source of a mass spectrometer the ethanol molecule fragments so the main peak in the ethanol spectrum is not the molecular ion peak at 46 amu but the CH_3O^+ fragment at 31 amu. This peak is adjacent to the molecular ion peak O_2^+ at 32 amu, so to measure ppm levels of ethanol correctly we need to be able to measure a small peak at mass 31 next to a very large peak at mass 32. Ethanol does also produce a large $C_2H_5O^+$ fragment peak at mass 45 (51% of the 31 amu peak) but it tends to be overlapped by isotopes of CO_2.

The ability of a mass spectrometer to measure a small peak next to a large peak is known as its Abundance Sensitivity and is a key indicator of the quality of the mass spectrometer. AMETEK's Dycor quadrupole mass spectrometers have a unique mass filter construction; the proprietary geometric construction of quadrupole rods and alumina collars and spacers provides superior performance without the need for alignment components. This superior performance is demonstrated in the two screenshots in Figures 1a and 1b. Figure 1a shows an analog scan of the oxygen peak in air (concentration 20.9476%). Figure 1b shows air with the addition of ethanol at 400ppm.

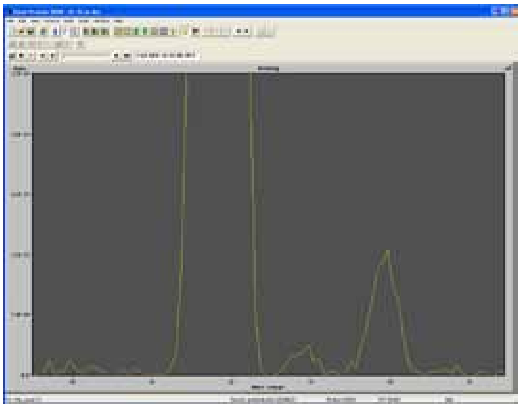

Figure 1a: Oxygen in air at 32 amu

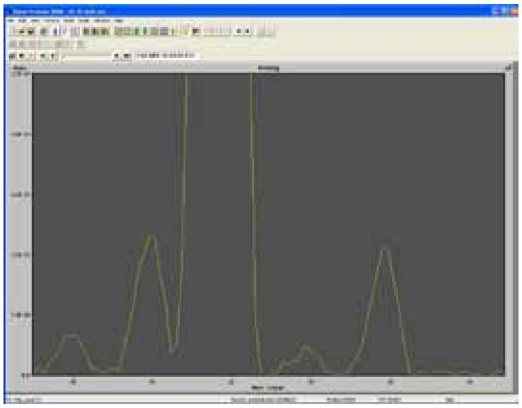

Figure 1b: Ethanol (400 ppm) at 31 amu, Oxygen in air at 32 amu

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The analyzer shows excellent abundance sensitivity, with the oxygen peak at mass 32 contributing less than 400ppb to the baseline of the ethanol peak at mass 31. In other analyzers this contribution can be many orders of magnitude higher and background corrections have to be applied to mass 31 to remove the influence of the 32 leading edge tail. This is unnecessary with the AMETEK mass spectrometers.

Precision and stability

To demonstrate the AMETEK mass spectrometer's ability to measure ppm levels of ethanol in air, a vaporizing system was set up to deliver a known stable concentration of ethanol in air to the mass spectrometer. Generally, calibration cylinders are used for this type of test but ethanol's low vapor pressure (only 44 mmHg at 20°C) makes it difficult to obtain high-pressure cylinders containing reasonable concentrations of the alcohol.

Instead, a known quantity of ethanol is evaporated into a known flowrate of carrier gas at a carefully controlled temperature; the concentration of ethanol in the carrier gas can be calculated easily and adjusted by adjusting the carrier gas flow.

An AMETEK MS was set up to monitor 400ppm ethanol in air for an eight hour period. The results are shown in Figure 2, with the statistical analysis of the data shown in Figure 3.

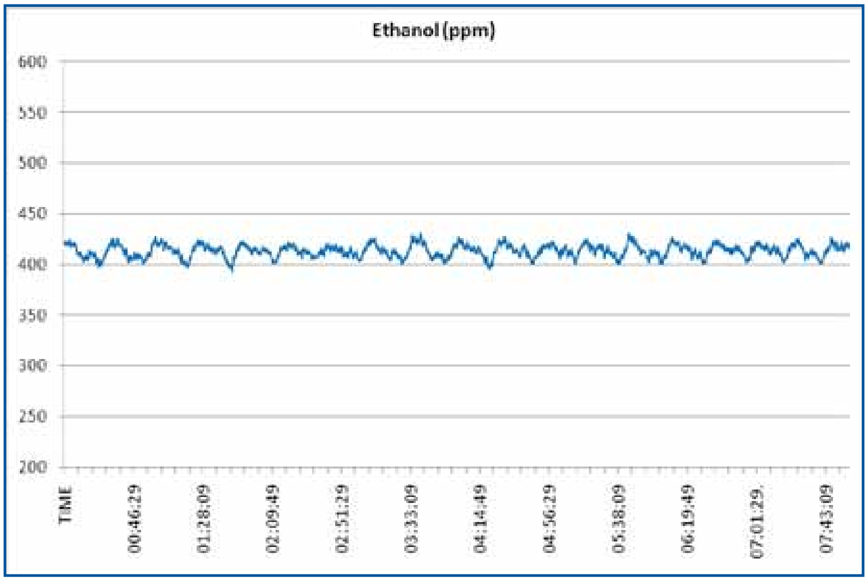

Figure 2: Analysis of 400 ppm Ethanol in air over eight hours on AMETEK Mass Spec

Average Reading over 7 hours (ppm)	413.29
Standard Deviation Absolute (ppm)	6.28
Standard Deviation Relative (%)	1.5

Figure 3: Statistical report on Ethanol analysis

Summary

The high performance of the AMETEK mass spectrometer means it is able to separate ppm levels of ethanol from percentage levels of oxygen. In the example above, 400ppm ethanol was measured over eight hours with a Relative Standard Deviation of just 1.5%. It is therefore able to provide accurate, precise quantitative analysis, making it ideal for continuous monitoring of processes in both the pharmaceutical and biofuel industries.

For more information on the AMETEK ProLine and ProMaxion process mass spectrometers, please contact the nearest AMETEK office or visit www.ametekpi.com.

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