Application Note AN-C-193

Alkyl amines in scrubber solutions

Determination of ethanolamines and methylamines besides inorganic cations for process monitoring

Scrubber solutions often contain mixtures of alkyl amines. These substances neutralize acidic harmful gases such as H_2S and CO_2, and remove them from industrial processes, which is known as «gas sweetening». In many industrial processes such as in oil refineries or natural gas production, this gas scrubbing treatment is crucial to inhibit corrosion and damage to piping and equipment from acidic gases. Additionally, such matrices are often very complex and can contain inorganic cations in higher concentrations as heat stable salts. Beside their use as corrosion inhibitors, ethanolamines and methylamines are used as raw materials for various production processes, e.g., detergents, emulsifiers, polishes, or for pharmaceuticals and chemical intermediates. Ion chromatography provides an effective means to monitor such processes. Good peak resolution and the separation of amines from inorganic cations is required. The high-capacity Metrosep C 6 column provides excellent conditions: narrow peaks as well as high flexibility in eluent compositions. This Application Note shows the method development for analysis of ethanolamines, methylamines, and common inorganic cations.

BACKGROUND

Harmful acidic gases form weak acids when transferred into an aqueous medium. They can react with weak bases, like ethanolamines in scrubber solutions, and transform into inert salts. Adding the appropriate amount of amines will neutralize the solution. In order to hold the pH value in an optimal range, a tight control of the chemical composition is necessary. Ion chromatography with conductivity detection provides an effective means to monitor this process and to control amine addition.

EXPERIMENTAL

The determination of cations and amines is performed as a non-suppressed analysis with a 940 Professional IC at 30 °C.

A mixture of nitric acid, dipicolinic acid, and acetone serves as mobile phase. Samples are injected with a 20 µL injection volume. Separation takes place on a Metrosep C 6 - 150/4.0 column equipped with a Metrosep RP 2 Guard/3.5. The conductivity signal is recorded and quantified with the MagIC Net software.

Column temperatures, flow rates, and eluent composition were varied to find an optimal peak resolution within the shortest possible analysis time (Table 1).

Table 1. Adjustments during method development to shorten run time and to increase peak resolution.

Parameter	Effect
Temperature increase	Shorter retention times, especially for alkaline earth metals
Flow rate increase	Faster elution with sharper peaks, with separation quality unchanged
Dipicolinic acid modifier	Divalent cations accelerate, magnesium and calcium change elution order
Acetone modifier	Improved resolution of amines

RESULTS

Ethanolamines and methylamines are well separated from various alkali and alkaline earth metal cations in less than 25 minutes (resolutions above 1.6 with 10 mg/L of each analyte) (Fig. 1).

The good resolution of sodium and ammonium (resolution greater than 3.1) allows their precise quantification beside the amines, even when one of the components occurs in great excess.

Thanks to the high capacity of the Metrosep C 6 - 150/4.0, larger volumes can also be injected without compromising the peak shapes. The column length allows the determination of these multiple compounds in a reasonable time of less than 25 minutes. In case of higher concentrations, resolution can be maintained by increasing the column length to a 250 mm column. Additionally, Inline Dilution can be used for automation of the dilution procedure to guarantee a proper resolution and quantification of all peaks.

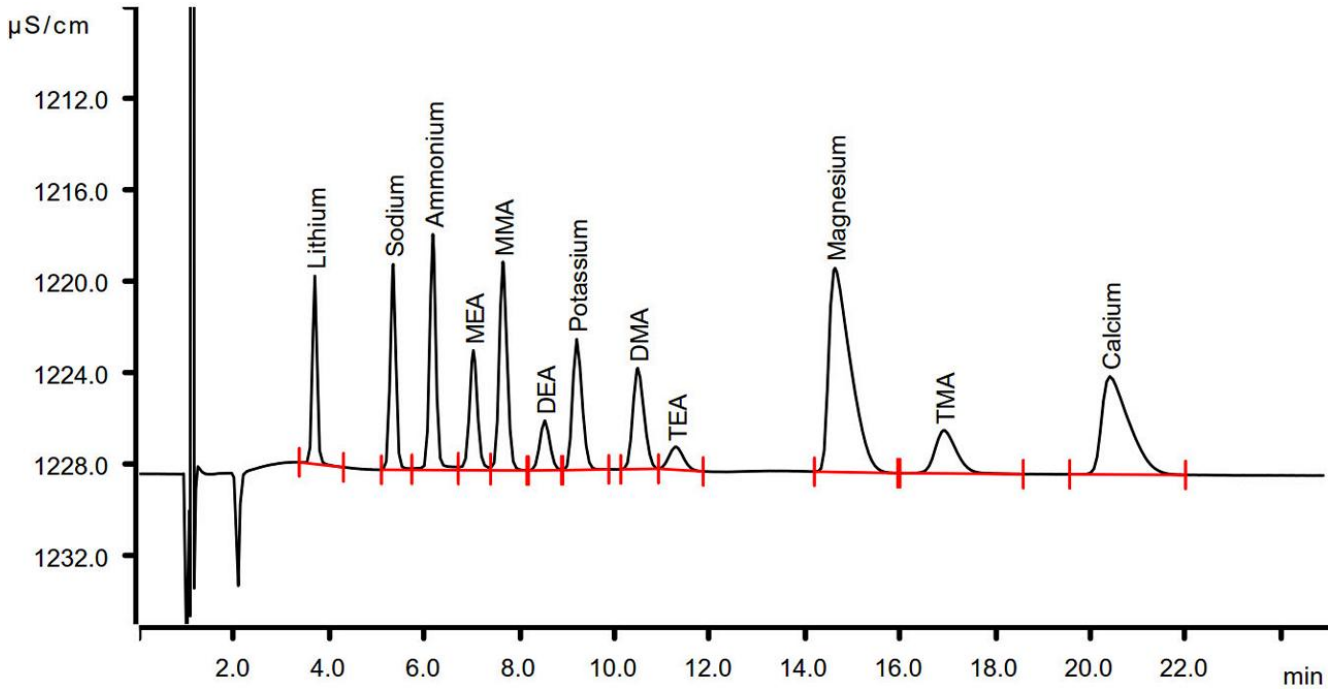

Figure 1. Determination of mono-, di-, and trimethylamine (MMA, DMA, TMA respectively) as well as mono-, di-, and triethanolamine (MEA, DEA, TEA respectively) besides lithium, sodium, ammonium, potassium, magnesium, and calcium in a mixed solution with a concentration of 10 mg/L.

CONCLUSION

Non-suppressed cation analysis with direct conductivity detection is a straightforward and robust technique which can be used at laboratory scale but also for process analysis. The 2060 Ion Chromatograph from Metrohm Process Analytics is therefore a reliable, highly precise automated solution (Fig. 2). These robust instruments for online process monitoring and control can be connected to up to 20 process points. Thus a sequential analysis at multiple areas inside of a plant is possible.

The application can be upgraded with further addons to further improve usability and automation:

- Dialysis or ultrafiltration as automated inline sample preparation techniques.
- MiPT for optimal injection volume, to cover a larger concentration range and to perform automatic calibration.
- Suppressed cations analysis for very low concentrations, to achieve an even better signal-to noise ratio.
- Mass spectrometry as a second independent detector in series after the conductivity detector to improve detection limits and confirm peak identity.

Figure 2. Ion chromatographs for laboratories (left) and for process analytics (right).

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