Challenge

A robust and accurate method for CO_2 absorption monitoring in aqueous amine scrubbing solutions for CO_2 emission reduction is needed.

Solution

The multi N/C series TIC measurement offers an accurate, automated, and reliable method for CO_2 routine monitoring in amine absorption solutions.

TIC Determination in Amine Scrubbing Solutions for Efficiency Control of CO_2 Emission Reduction from Fossil Fuel Combustion

Introduction

Reducing carbon dioxide emissions and hence limiting global warming is a major challenge for present and future generations. Major CO_2 emitters in industry include fossil fuel-fired power stations, waste incineration plants, and cement/concrete production. In these industries, additional carbon capture and storage plants (CCS) can be installed to absorb the CO_2 from the flue gas and subsequently enable purification, liquefaction, and storage. Separation and recovery of CO_2 for reuse by conversion into valuable products with the goal of carbon neutrality is a big topic in industrial research and development of new technologies. Carbon dioxide capture plants typically use a liquid solvent, which catches the CO_2 in the absorption section (figure 1, right part) and releases it in a desorption part (figure 1, left part) before it is recycled to the absorption part.

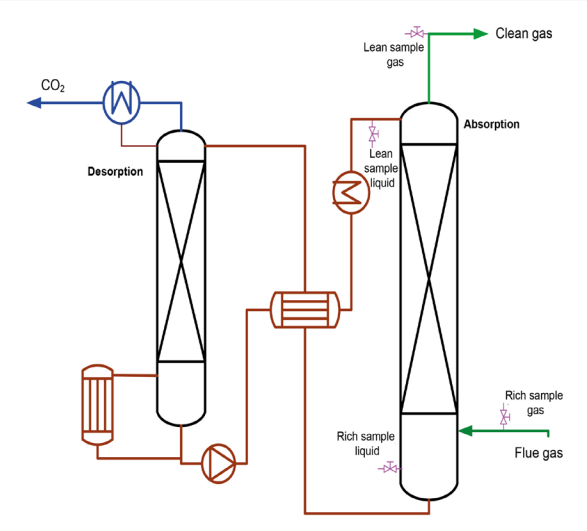

Figure 1: Sketch of a typical carbon dioxide capture plant

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These liquid solvents typically consist of aqueous amine solutions, such as 30% amine in water (e.g., monoethanolamine – MEA, 2-amino-2-methyl-1-propanol – AMP, and others), which react with the CO_2 in the absorption part and bind it chemically.

$$R\text{-}NH_2 + CO_2 + H_2O \leftrightarrow R\text{-}NH_3^+ + HCO_3^-$$

When heated up during the desorption process, the chemical bond is reversed, and almost pure CO_2 is released. However, heating is an energy-intense process and reducing the heat required can save a lot of operating costs. But reducing the heat input during desorption (lowering the desorption temperature) also means higher amounts of remaining CO_2 in the amine solvent, reducing absorption capability.
To find the optimum between absorption performance and required heating power, monitoring of CO_2 loading in the amine solution is very important and must therefore be measured on a regular basis. These measurements can be conducted by different methods, like Raman spectrometry, conventional titration or total inorganic carbon (TIC) analysis by a TOC/TIC analyzer.

Since the amine solutions are subject to aging due to thermal stress, the resulting decomposition and discoloration processes interfere with spectrometric measurement methods. However, instrumental TIC analysis has been shown to be unaffected by these changes and is therefore the method of choice for monitoring CO_2 loading to scrubber solutions.
In this application note, Analytik Jena's multi N/C 2100S analyzer was applied to measure CO_2 concentrations by a TIC method in the lean solvent – solvent with reduced CO_2 amount flowing to the absorption part – and in the rich solvent – solvent with high CO_2 concentration flowing to the desorption part. In addition, some samples were analyzed for comparison as well with a volumetric titration method that was used in the past. For this purpose, different lean and rich concentrated samples were taken after reaching a steady state at a test setup operated by Sulzer Chemtech Ltd., Switzerland. Here a synthetic flue gas, i.e. ambient air mixed with a known amount of CO_2 was fed to the absorption part. Gas samples at inlet and outlet were monitored for CO_2 concentrations continuously via NDIR gas analyzers.

Materials and Methods

The TIC determination was carried out by the multi N/C 2100S in combination with the autosampler AS 60 according to the TIC determination described in DIN EN 1484.

Samples and reagents

- 12 lean and rich samples each, from Sulzer Chemtech's test setup
- 10% phosphoric acid for automatic TIC determination
- TIC calibration standard solutions (sodium carbonate and sodium hydrogen carbonate in water)

Sample preparation and measurement

Lean liquid samples were diluted 1:30 with deionized water and rich liquid samples were diluted 1:100. Dilution ratio depends on the final CO_2 concentration and is targeted to 300–400 mg/L. All samples were filled into 8 mL sample vials, covered with aluminum foil and placed on the sampler tray.

For direct TIC measurement, a representative sample aliquot of 500 µL was fed by a microliter syringe into the TIC reactor of the analyzer. An aliquot of 10% phosphoric acid was automatically dosed into the TIC reactor. Through the acid, HCO_3^- is converted to CO_3^{2-} (the dissolved form of CO_2). The dissolved CO_2 is released from the solution by purging with the clean carrier gas (pure oxygen or synthetic air free of hydrocarbon and CO_2). The measurement gas was transferred to the detector after appropriate drying and purification. Quantification was performed using non-dispersive infrared spectrometry in a focus radiation NDIR detector.

Calibration

The multi N/C analyzer was calibrated with sodium carbonate and sodium hydrogen carbonate (50:50 mix) standard solutions for two concentration ranges of 5–50 mg/L and 50–500 mg/L TIC.
All calibration solutions were prepared according to DIN EN 1484. In both ranges a linear calibration function was used.

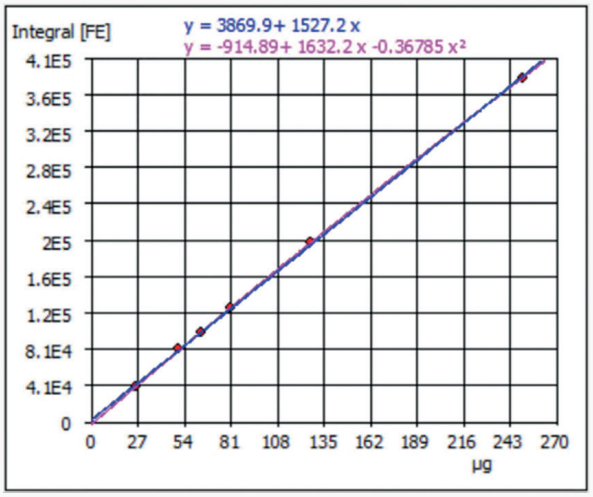


Figure 2: Example of a calibration curve TIC 50–500 mg/L

Method settings

Table 1: Method settings for multi N/C 2100S

Parameter	Specification
Method of determination	TIC
Sample digestion	10% H_3PO_4
Number of replicates	min. 2, max. 3
Autosampler, rack and vial size	AS 60, 60 position rack, 8 mL sample vials
Rinse cycles with sample	3
Injection volume	500 µL
Integration time	240 s

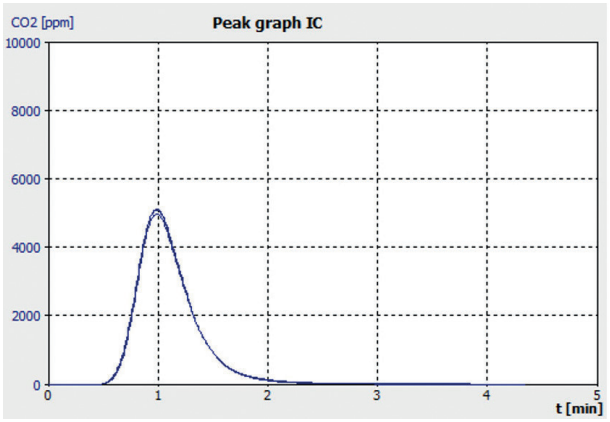
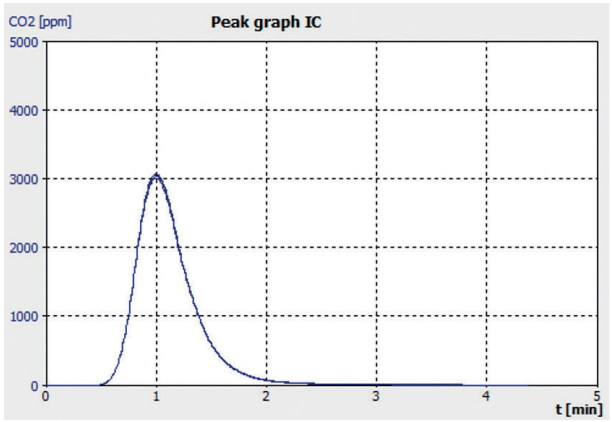
Results and Discussion

Examples of analytical results are given in Table 2 and Table 3. TIC measurements were each carried out as multiple injections from a sample vessel. Pairs of lean and rich samples were taken at different column operating conditions. In comparison, samples were analyzed by standard titration method, too. Due to the big manual effort in titration, only analysis of the sample "Lean 2" was repeated. Here, the standard deviation is about 10 times higher than found in TIC analysis.

Table 2: Result comparison of TIC and titration method for lean and rich samples

Sample ID	Results TIC (dilution) ± SD [mg/L]	Dilution ratio	CO_2 concentration by TIC method ± SD [%-wt]	CO_2 concentration by titration method ± SD [%-wt]
Lean 1	338.2 ± 0.94	1:30	3.489 ± 0.010	2.922
Rich 1	293.7 ± 0.28	1:100	9.683 ± 0.009	13.841
Lean 2	450.3 ± 3.75	1:30	4.875 ± 0.032	4.212 ± 0.34
Rich 2	271.8 ± 2.42	1:100	8.989 ± 0.080	9.233
Lean 3	465.7 ± 1.30	1:30	4.714 ± 0.013	4.034
Rich 3	280.2 ± 1.10	1:100	9.313 ± 0.037	8.883

Table 3: Examples of measurement curves for lean and rich samples

Lean 2	Rich 2
	

The example measurement curves illustrate the excellent reproducibility of the measured values within a multiple injection from a sample vessel. As a result, the TIC method shows the lowest deviation to the known amount of added CO_2 and also the lowest standard deviation in comparison of the analysis methods.
NDIR analysis of the gas phase is a little less accurate but is beneficial due to its online concentration availability. However, titration of the liquid samples shows the worst accuracy with the biggest standard deviation.

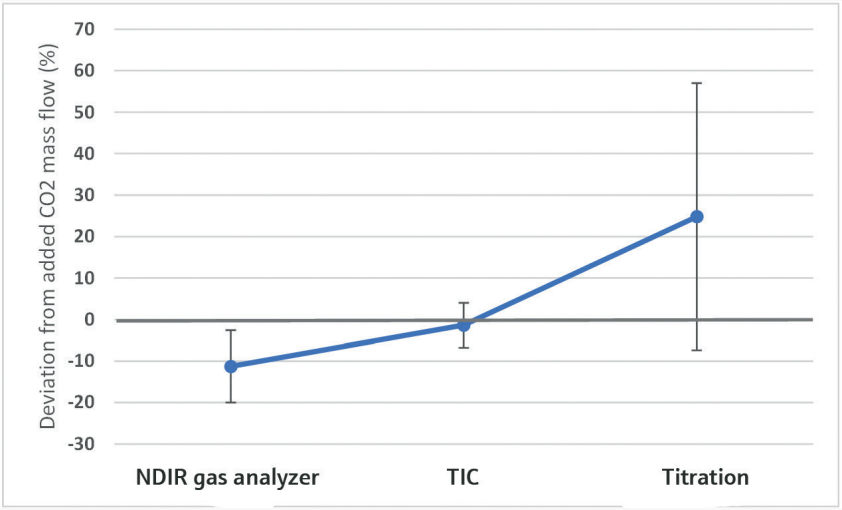


Figure 3: Comparison of the deviation of results of different measurement methods from the nominally added CO_2 concentratoin to the exhaust gas and respective measurement uncertainty (vertical deviation bars)

Conclusion

TIC measurement with the multi N/C series provides a very robust method for determination of CO_2 concentrations in absorption solvents for reducing CO_2 emissions from fossil fuel incineration processes. As shown by the measurement data, the method achieves a very good accuracy of results with very low standard deviation. In comparison to other methods, less manpower and sample preparation effort is required, which is an additional economic benefit.
The direct injection TOC analyzer multi N/C 2100S with the AS 60 autosampler offers the advantage of very low sample consumption per analysis. Less than 5 mL of sample is typically sufficient for a triplicate determination of the TIC parameter. Whereas the multi N/C 3100 flow injection TOC analyzer equipped with the AS vario + dilution rack even offers the automation of the mentioned dilution ratios of original samples from 1:5 to 1:100 and thus a higher operation comfort.
Both multi N/C analyzers are well suited to support the TIC/CO_2 concentration monitoring in amine absorption solutions. In addition, they can be used for the amine concentration measurement in these aqueous absorption solutions by a direct TOC/TN_b determination, if the analyzer is equipped with an additional nitrogen detector, like electrochemical detector (ChD) or chemoluminescence detector (CLD).

Figure 4: multi N/C 2100S

References

[1] DIN EN 1484: 2019-04 Water analysis – Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC)

Acknowledgements

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