TXRF

Fast analysis of Benfield process solutions by TXRF spectroscopy

Application Note # XRF 459

Introduction

The Benfield process is a technique which is used for the removal of CO_2 and H_2S from natural and industrial gases. Main application fields are:

- Natural gas treatment to achieve liquid natural gas (LNG) or pipeline specification.
- Synthesis gas treatment for CO_2 removal in ammonia plants.
- Synthesis gas treatment for CO_2 removal in iron ore direct reduction plants.
- Recycle gas purification in ethylene oxide facilities.

The schematic Benfield process is shown in Figure 1. It is divided into a gas absorption step and a subsequent regeneration of the absorbant.

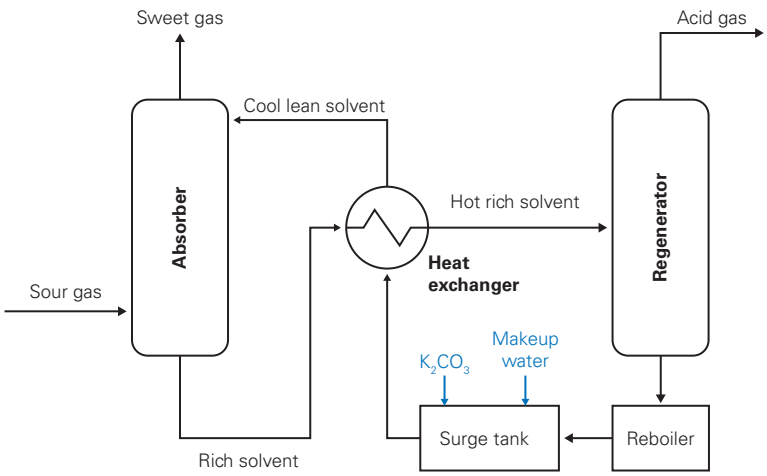

Figure 1
Basic Benfield process – schematic

Benfield process

The gas compounds to be removed from industrial gases react with the potassium carbonate in the absorption solvent:

$K_2CO_3 + CO_2 + H_2O \rightarrow 2\ HCO_3^- + 2\ K^+$

$K_2CO_3 + H_2S + H_2O \rightarrow HCO_3^- + HS^- + 2\ K^+$

The spent solvent is steam-stripped of the absorbed CO_2 and H_2S in the regenerator. The regenerated solvent is recycled back to the absorber after recovering the energy by use of heat exchangers. To prevent corrosion vanadium is added to the absorption solvent. Additionally side stream solids are accumulated. These contain the absorbed elements, which in case of natural gas treatment can be heavy metals including mercury.

A major analytical challenge for natural gas production is the remote location of most sites and analytical facilities, which makes the supply of technical gases or cooling water a challenge. In industrial environments the main demand on analytics is a quick turnaround of measurement results. Therefore, it is highly appreciated if sample preparation and analysis can be performed close to the production site.

Element	Conc. [mg/kg]	s [mg/kg]	LOD [mg/kg]
P	405	63	94
S	63534	2594	55
K	40623	1179	14
Ti	35	7.7	4.4
V	8402	226	3.3
Cr	1637	63	3.2
Mn	471	13	3.0
Fe	129913	4716	3.0
Ni	516	20	0.82
Cu	175	8.3	0.71
Hg	16295	749	0.93

Table 1
TXRF measurement results for the side stream solid sample (s = standard deviation of a sevenfold measurement, LOD = limit of detection).

The main tasks of the Benfield process are the control of the potassium concentration as main factor for the absorption potential of the solution and the determination of vanadium for corrosion prevention. In addition the side stream solids must be analyzed with particular

Sample	K [mg/l]			K_2CO_3 [wt%]	V [mg/l]			V [wt%]	S [mg/l]	
	TXRF		ICP-OES	Wet chemistry	TXRF		ICP-OES	Wet chemistry	TXRF	
	Average	s	Average	Average	Average	s	Average	Average	Average	s
513888	26076	5836	24000	53.3	782	100	760	1.000	< LOD	–
513889	28191	4098	27000	54.1	898	55	810	0.919	< LOD	–
598101	19082	1719	15000	15.1	470	25	510	0.619	2806	365
598104	18457	1639	16000	18.0	470	25	470	0.611	2115	185
598105	23274	1803	16000	38.5	535	54	520	–	89	15
598106	14739	679	13000	20.0	360	18	420	–	1764	69
598107	15917	970	12000	19.1	340	45	420	–	1897	64
598108	18799	1017	15000	15.8	429	32	490	0.587	2631	197

Table 2
Measurement results derived from TXRF, wet chemistry and ICP-OES analysis for potassium, vanadium and sulfur in Benfield process solutions (s = standard deviation of a sevenfold measurement).

attention to the toxic metals. General analytical challenges are the high matrix concentrations of the solvents and the variable element distributions of the side stream solids.

Sample preparation

Eight fresh or used potassium carbonate solutions and one side stream solid sample from the Moomba gas field in Central Australia were kindly provided by Santos Ltd.

1 ml aliquots of the Benfield solutions were diluted with 10 ml of double-distilled water. 100 µl of a scandium solution (1 g/l) were added for internal standardization. After thorough homogenization 10 µl sample solution were pipetted onto a quartz glass sample carrier and subsequently dried on a hot plate at 60 °C (140 °F).

The dry side stream solid sample was carefully ground in an agate mortar for 2 min. 100 mg of the ground material were weighed into a centrifugation tube and suspended in 5 ml of an aqueous Triton X-100 solution (1 Vol.-%). 10 µl of a gallium solution (1 g/l) were added for internal standardization. After thorough homogenization the centrifugation tube was fixed in an automatic sample shaker and 10 µl of the sample suspension were transferred to siliconized quartz glass sample carriers while the sample was shaken at ~800 r/min. For determination of the analytical reproducibility samples were prepared sevenfold.

All samples were measured with the S2 PICOFOX spectrometer, equipped with a Mo microfocus tube and a 30 mm^2 XFlash® silicon drift detector. Tube settings were 50 kV/600 µA. Measurement times were 180 s for the Benfield solutions and 1000 s for the side stream solid, respectively.

The TXRF results were compared with wet chemistry data for potassium (or potassium carbonate) and vanadium provided by Santos Ltd. and with ICP-OES measurements from an external service laboratory.

Results

The results for the side stream solid and the Benfield process solutions are summarized in Table 1 and Table 2, respectively. Figure 2 shows the potassium concentrations from TXRF and external ICP-OES measurements compared to the K_2CO_3 values measured by wet chemistry.

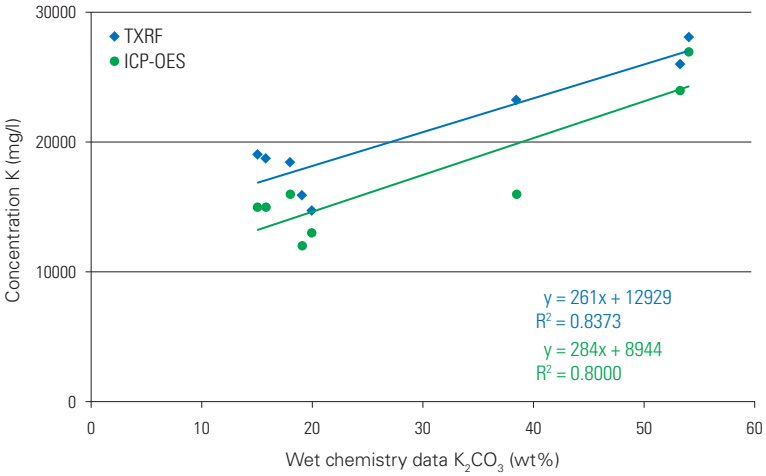

Figure 2
Comparison of TXRF and ICP-OES values for potassium with wet chemistry data for potassium carbonate in Benfield process solutions.

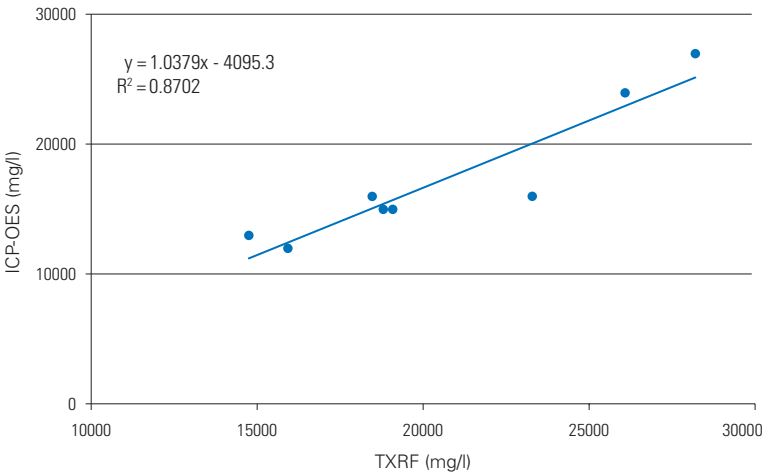

Figure 3
Comparison of TXRF and ICP-OES values for potassium in Benfield process solutions.

For both methods a linear concordance with the K_2CO_3 values can be observed, but systematic deviations of the absolute amounts are obvious. This is most probably caused by a completely different sampling and analytical approach. Figure 3 clearly shows the good concordance of the TXRF and ICP-OES results.

For the determined vanadium concentrations a very good concordance of wet chemistry

data on one hand and of TXRF and ICP-OES values on the other hand is shown in Figure 4. This can also be observed when TXRF and ICP-OES values for vanadium are compared (Figure 5).

For sulfur there are no comparative values from other measurement methods. Nonetheless, it can be stated that the simultaneous analysis of this element by means of TXRF is possible with good reproducibility.

In addition to the Benfield process elements described here, high amounts of iron and mercury as well as traces of titanium, chromium, manganese, nickel and copper were detected in the side stream solid sample.

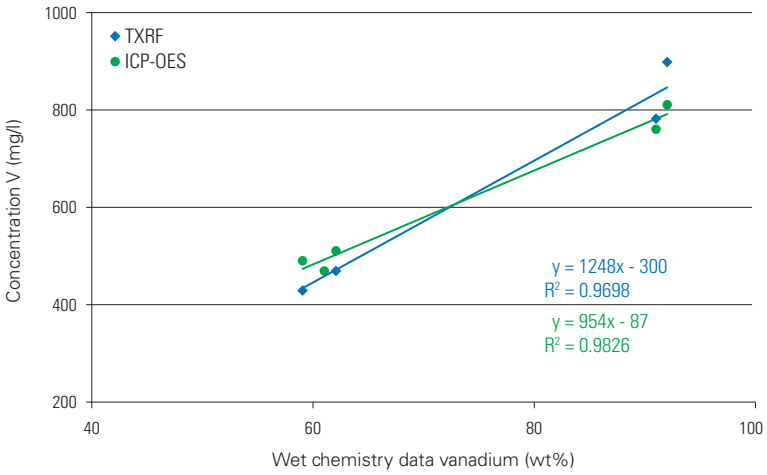

Figure 4

Comparison of TXRF and ICP-OES values for vanadium with wet chemistry data for vanadium in Benfield process solutions.

Conclusion

TXRF was proven to be a suitable analytical tool for the fast analysis of potassium, vanadium and sulfur in Benfield process solutions. The applied sample preparation only requires a simple dilution step with water, internal standardization with a mono element solution and drying of a small aliquot on a sample carrier.

The straightforward preparation procedure in combination with a comparably low demand for a laboratory infrastructure promotes TXRF to an ideal analytical technology for the operation in small laboratories or at remote locations.

Moreover, complicated samples like side stream solids can be analyzed by TXRF with minimum of sample preparation and operation expense.

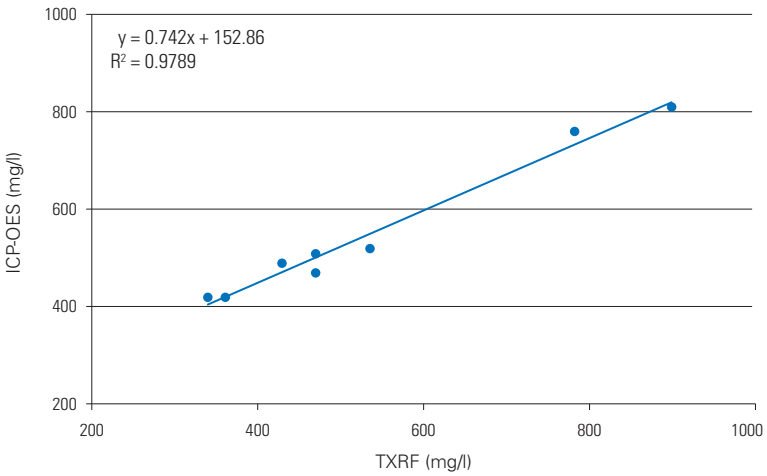

Figure 5

TXRF and ICP-OES values for vanadium in Benfield process solutions.

Author

Hagen Stosnach, Bruker Nano GmbH, Berlin, Germany

All configurations and specifications are subject to change without notice.
Order No. DOC-A81-EXS059, Rev.2.1 © 2015 – 2025 Bruker Nano GmbH, Am Studio 2D, 12489 Berlin, Germany.

Bruker AXS
Info.baxs@bruker.com

www.bruker.com/s2-picofox