

REFINERY TRIAL OF AN INFRARED BAYER LIQUOR ANALYSIS SYSTEM

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ABSTRACT

The chemical analysis of Bayer liquor is a critical requirement for the control of the Bayer process. Knowledge of these parameters is needed to keep Bayer liquors within set limits, which maximise the efficiency of unit processes such as bauxite digestion, aluminium hydrate crystallisation, and causticisation. A ground breaking infrared-based method for Bayer liquor analysis which requires no titrations, liquor dilution or additional reagents has been successfully trialled over a number of months in several alumina refinery laboratories. The method is fully automated and capable of analysing a range of liquor components including alumina, total caustic, total alkalinity, total organic carbon (TOC) and oxalate, along with a range of other organic and inorganic compounds.

Liquor samples from across the entire Bayer process were analysed daily by both currently used routine analysis methods and infrared. The total alumina, total caustic, total alkalinity, TOC and sodium oxalate results from one refinery were compared. The results from the infrared-based system were effectively the same as those obtained from the current routine methods of analysis, except far more detail was available using the trialled commercial infrared-based system. Correlation coefficients between the infrared-based system and routine titrations were typically greater than 0.999 for the alumina, total caustic and total alkalinity results. For the TOC and sodium oxalate results, correlation coefficients were typically greater than 0.995. The analysis time for the infrared-based measurements is substantially shorter than current methods. No fouling of the infrared analyser was observed over the course of the trial. The use of infrared for liquor analysis will undoubtedly provide major benefits to the alumina industry.

1. INTRODUCTION

Aluminate, caustic and carbonate concentrations are used to control the Bayer process and optimise digestion, crystallisation and causticisation. Oxalate and Total Organic Carbon (TOC) levels provide information to allow process adjustments based on the organics load.

Classic titration methods are used for the measurement of aluminate, caustic and carbonate in Bayer liquors. For decades the gluconate-fluoride titration method of Watts and Utley (1953, 1956) has formed the basis for Bayer liquor analysis. This method has been adapted and automated over the years (Connop and Morton, 1997; Gran, 1952; Johansson and Gran, 1980; Magrone et al., 1978; VanDalen and Ward, 1973).

Titration based techniques require accurate sample delivery and dilution systems with well maintained electrodes. Titrations are time consuming and generally provide information limited to total alumina (A), total caustic (C) and total alkalinity (S). Further analytical techniques are required for other measurements.

Bayer liquor analysis by infrared (BLAIR) is a spectroscopic system that provides rapid and comprehensive analyses in a single measurement (Patrick et al., 2014, Karakyriakos et al., 2015). The BLAIR analysis suite includes A, C, S, oxalate, TOC, acetate, formate, succinate, malonate, chloride, sulfate, total sodium and density.

This work presents the results from a BLAIR system trial at the Queensland Alumina (QAL) Gladstone refinery. Measurements of process liquors from across the entire Bayer process were analysed on a daily basis and compared with results from current routine methods.

2. EXPERIMENTAL

Bayer Technologies set up an automated BLAIR system (Figure 1) for use at the QAL refinery process laboratory.

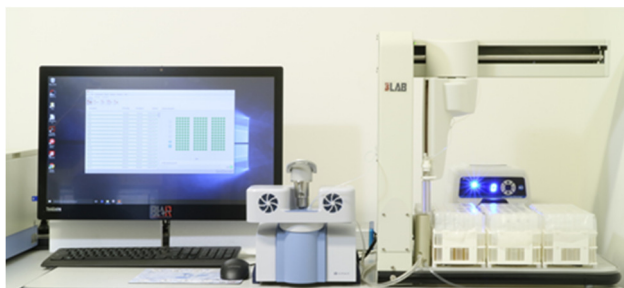


Figure 1. BLAIR system

The BLAIR system operates over a range from low A/C liquors similar to process water up to full strength high A/C green liquors.

The trial was held over several months using process liquor samples from across the entire QAL Gladstone refinery.

More than 700 Bayer liquor samples were analysed using both BLAIR and the current routine methods of analysis. The BLAIR and routine analysis method values for aluminate, total caustic, total alkalinity, oxalate and TOC were compared.

3. RESULTS AND DISCUSSION

The correlation between the BLAIR and reference method results is shown in Figures 2 to 5. The solid lines in these figures are the $y=x$ lines. The BLAIR results were recorded using a Normal Mode measurement setting. These normal mode measurements require approximately three minutes per measurement. Along with A, C, S, A/C, C/S, oxalate and TOC used in the direct comparison, the additional species of acetate, formate, succinate, malonate, sulfate, chloride and total sodium were also determined, as well as density and the breakdown of organics (BORG) factor.

An excellent correlation between the BLAIR and current routine methods of analysis was observed. The correlation coefficients (R) for each parameter along with the root mean square error (RMSE) are given in Table 1. For sodium oxalate, above an inflection point of 6 g/L, the BLAIR oxalate results were slightly lower than the QAL reference method values. The BLAIR oxalate results at these higher concentrations were typically 0.8 g/L lower than the QAL reference method values. In the 0 to 5 g/L oxalate concentration range the BLAIR and reference method results were well matched with an average difference of less than 0.2 g/L.

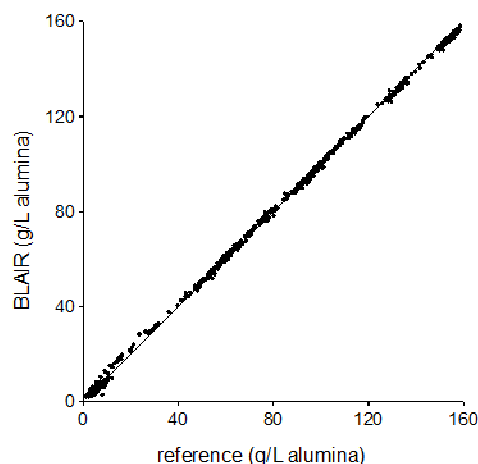


Figure 2. Results for total alumina (A)

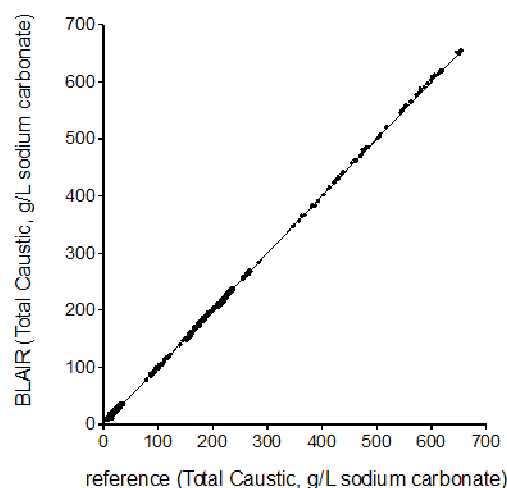


Figure 3. Results for total caustic (C)

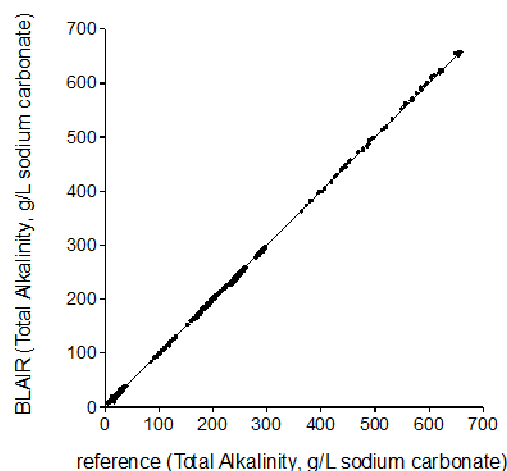


Figure 4. Results for total alkalinity (S)

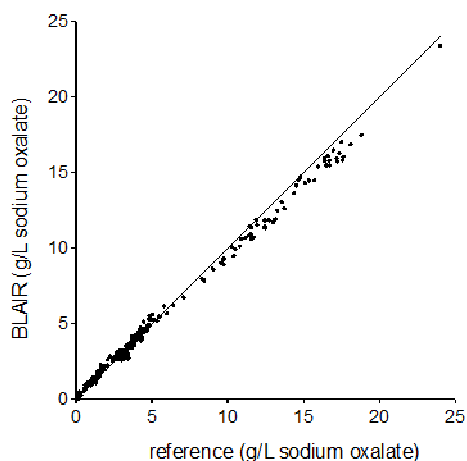


Figure 5. Results for sodium oxalate

Table 1. R and RMSE Values

	A	C	S	Ox	TOC
R	0.9997	0.9998	0.9998	0.9980	0.9984
RMSE	1.2	2.5	2.8	0.4	2.1

RMSE units- A:g/L alumina, C and S: g/L sodium carbonate, Ox: g/L sodium oxalate and TOC: g/L organic carbon.

To quantify the precision of the method, the standard deviations for forty replicate measurements of a low A/C synthetic liquor (A/C= 0.202) and ten replicate measurements of a high A/C synthetic liquor (A/C = 0.758) have been determined by Bayer Technologies. Table 2 compares these values with the standard deviations from the literature for twenty replicate titration measurements of a liquor with an A/C ratio of 0.419 (Connop and Morten, 1997).

Table 2. Standard Deviations

	A	C	S	A/C	C/S
BLAIR low A/C	0.25	0.47	0.47	0.0008	0.0012
BLAIR high A/C	0.26	0.41	0.47	0.0005	0.0008
Titration*	0.26	0.55	0.59	0.0008	0.0023

* Connop and Morten, 1997

The results in Table 2 show that the precision of the BLAIR system for A, C, S, A/C and C/S is similar and in some cases better than the referenced classical titration method. These BLAIR measurements were recorded using a

Precise Mode setting which requires approximately ten minutes for a full analysis. The typical standard deviations for oxalate and TOC using the Precise measurement mode were 0.05 g/L and 0.19 g/L respectively.

The standard deviations for the BLAIR measurements remain relatively unchanged with increasing concentration. The BLAIR low A/C liquor has an A of 50 g/L, C of 248 g/L and S of 268 g/L. On increasing these values to an A of 230.5 g/L, C of 303.9 g/L and S of 305.7 g/L the standard deviations remained relatively unchanged (see Table 2).

Over the course of the trial there was no evidence of any fouling of the BLAIR system. Areas in regular contact with a range of Bayer liquors showed no signs of scaling. The BLAIR system performs a series of automatic wash and flush cycles which prevent any fouling.

4. CONCLUSION

An advanced infrared-based Bayer liquor analysis system (BLAIR) trialled in an alumina refinery process laboratory gave results for total alumina, total caustic, total alkalinity, sodium oxalate and TOC which correlated closely with current methods of analysis.

The measurement precision for BLAIR was equivalent to and in some cases better than those reported from classical titration methods (Connop and Morton, 1997).

The measurements required less time and resources than the current methods of analysis and delivered a comprehensive suite of analytes including alumina, total caustic, total alkalinity, oxalate, TOC, sulfate and chloride. Other organic species also regularly determined by BLAIR included acetate, formate, malonate and succinate.

Very little maintenance was required for the BLAIR system over the course of the trial. With the inbuilt wash and flush cycles no fouling of the sample lines or any other system components was observed making it remarkably robust.

This trial shows that BLAIR is capable of providing accurate and precise process liquor information. All of this information is provided in a fraction of the time currently required. Recent, ongoing improvements to the BLAIR system have shown a propensity to increase this accuracy and precision even further, making timely and finer control possible at the plant level.

5. ACKNOWLEDGEMENTS

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