

DETERMINATION OF THE SODIUM CONTRIBUTION OF SOLVENT-EXTRACTABLE ORGANIC COMPOUNDS IN BAYER PROCESS LIQUOR

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Abstract

A thermometric titrimetric procedure has been developed to determine the sodium contribution of solvent extractable organic compounds in acidified Bayer process liquor. The precision of the method is estimated to be 0.2% RSD.

Introduction

The majority of organic compounds in Bayer process liquor are present as their sodium salts. Knowledge of the sodium contribution of organic compounds in Bayer process liquor is important in seeking causes for organic-related process disturbances, evaluating the effect of processes to remove these compounds and closing sodium mass balances. Modern chromatographic procedures such as high performance liquid chromatography (HPLC) and ion chromatography (IC) permit the quantitative determination of lower molecular mass organic compounds, and it is easy to compute the sodium contribution of these compounds to the total sodium content of the liquor.

Higher molecular mass organic species have been implicated in a variety of Bayer process disturbances. However, speciation and quantification of these compounds present greater challenges, and it is difficult to apportion the sodium contribution that these compounds make to the total sodium content of the liquor. This is so particularly in a process control environment where simpler, more robust analytical instrumentation is preferred.

It is well known that a considerable proportion of these higher molecular mass compounds may be extracted into certain non-aqueous solvents after the liquor has been acidified. It was considered that the gross acid value of the extractable organic compounds could be determined by a non-aqueous titration with standard base in a suitable alcohol. By knowledge of the amount of base consumed in the neutralization titration, the total sodium contribution of these extractable organic compounds could be determined. Potentiometric titrations in non-aqueous media present a number of challenges for the analyst. These include the dehydration of the necessarily hydrated glass membrane of the pH electrode, the poor electrical conductivity of such non-aqueous solutions, the frequent and rapid fouling of both the glass membrane and the reference electrode and the sensitivity of the very high impedance pH signal to static electrical disturbances.

Thermometric titrimetry offers obvious advantages over potentiometric titrimetry in non-aqueous media, the relatively low impedance sensor requiring no electrical contact with the titration media. However, the reaction enthalpy of base with many weakly acidic species in non-aqueous media is low, and endpoints are often indistinct and imprecise. Several thermometric titration techniques involving catalytic indicators have been developed to enhance endpoints (Vaughan and Swithenbank 1965 in Vaughan, 1973, Smith 2003), but none of these has been proven to have wide ranging industrial application.

A thermometric titrimetric procedure has been developed recently for the determination of free fatty acids (FFA) in edible oils from exotic plants (Carneiro *et al.*, 2002), and this has been extended to cover the determination of FFA in a range of other plant and animal fats and oils (Metrohm, 2006). The procedure has also been found to be very satisfactory for the determination of weakly acidic species in mineral oils as Total Acid Number, or TAN (Metrohm, 2007). By using a catalytic endpoint indicator,

Carneiro *et al.* showed that sharp, highly reproducible endpoints could be obtained from titrations which otherwise would have revealed little or no inflection at the endpoint. The catalytic indicator is paraformaldehyde, which undergoes an endothermic depolymerization with the first trace of excess hydroxyl ions after all acidic species have been neutralized.

This work reports on the successful application of this technique to the determination of extractable weakly acidic species in Bayer process liquor.

Experimental

Equipment:

- Metrohm 859 Titrotherm thermometric titration interface module
- Metrohm 800 Dosino with 10mL burette
- Metrohm 802 overhead stirrer, with 804 titration stand
- Metrohm 6.9011.020 Thermoprobe thermometric titration probe
- Metrohm 6.1415.220 glass titration vessel, 90mL.

Titration operating software:

- Metrohm Titrotherm thermometric titration software, v. 1.0

Reagents:

- Titrant: 0.1mol/L potassium hydroxide in propan-2-ol, prepared from A.R. reagents
- Paraformaldehyde, powder, 95% - Sigma-Aldrich cat. no. 158127
- Benzoic acid, min. 99.5%, Sigma-Aldrich cat. no. B-3250
- Hydrochloric acid, 32% w/v, A.R. grade
- Cyclohexanol, 99%, Sigma-Aldrich cat. no. 105899
- Propan-2-ol, A.R.
- Saturated sodium chloride solution.

Samples:

Experiments were conducted on two samples of spent Bayer process liquor supplied by two Australian alumina refineries.

Methodology:

A 25mL of spent Bayer liquor is pipetted into a 400mL beaker, and diluted with 125mL D.I. water. Allow 10 minutes for the pipette to drain properly, due to the viscous nature of the liquor. Place on a stirrer, and while stirring, carefully neutralize and then acidify with 32% w/v hydrochloric until the solution is clear. Cool the solution, and transfer to a 250mL separating funnel.

Extract this solution with 5 x 25mL aliquots of cyclohexanol, allowing adequate time after each extraction for a full separation of the two phases. Return the collected cyclohexanol extract to a clean separating funnel, and wash with 10 x 50mL amounts of saturated NaCl solution (this aids phase separation, and reduces solubility of cyclohexanol). Quantitatively transfer the washed cyclohexanol extract to a 200mL volumetric flask, and make to

volume with cyclohexanol. Dry the solution overnight in a sealed container with 50g anhydrous Na_2SO_4 freshly dried at 120°C using a magnetic stirrer to ensure efficient drying.

Depending on the organic content of the original liquor, transfer 25 to 40mL of the dried cyclohexanol extract to a 200mL volumetric flask, and make to volume with dry A.R. propan-2-ol. Allow 10 minutes for the pipette to drain properly due to the viscous nature of the fluid.

Pipette a 30mL aliquot into a titration vessel, allowing to drain for a timed 3 minutes due to the viscous nature of the fluid. Add approximately 0.5g of paraformaldehyde, and titrate to a thermometric endpoint with 0.1 mol/L potassium hydroxide in propan-2-ol.

Basic titration parameters (applicable to Metrohm 859 Titrotherm only)

Titrant delivery rate (mL/min)	2
No. of exothermic endpoints	1
Data smoothing factor	75
Stirring speed (802 stirrer)	9
Delay before start (secs)	3

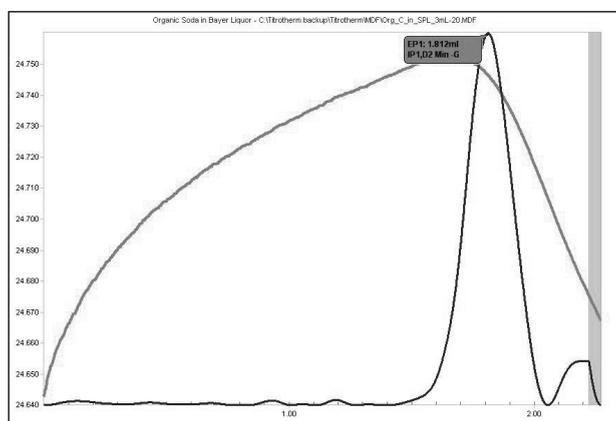
Results and Discussion

1. Replicate analysis of alumina refinery spent liquor, "organic soda contribution" as g/L Na_2CO_3

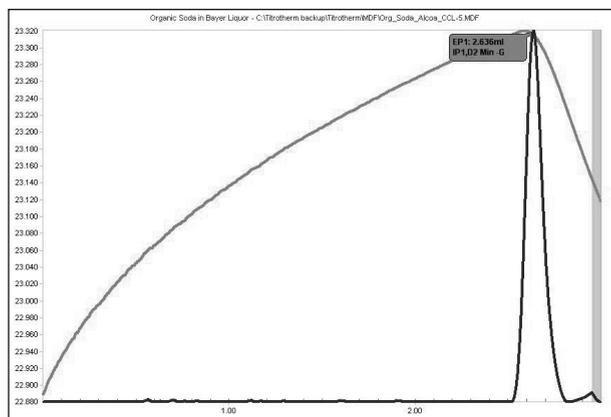
- From alumina refinery 1 9.92 ± 0.01 (n=6)
- From alumina refinery 2 18.37 ± 0.04 (n=6)

The analysis has been shown to be highly precise, and thus is very suitable for following process trends, as well as investigations into organic removal processes. However, this work needs to be followed by an investigation into the range of organic species which can be extracted under these conditions.

2. Thermometric titration plots



Alumina refinery 1



Alumina refinery 2

Figure 1. Titration of weakly acidic species extracted from alumina refinery process liquors

Red = direct temperature plot

Black = second derivative of direct temperature

Tags denote endpoint as determined from second derivative curve.

A comparison of typical titration plots illustrated in Figure 1 suggest that the spectrum of organic compounds extracted from the spent liquor from alumina refinery 1 might differ from that extracted from the liquor from refinery 2. This is suggested by the greater rounding of the endpoint, indicating greater non-equilibrium behaviour between the weakly acidic species and the titrant base at the endpoint. Such non-equilibrium behaviour does not affect the ability of the thermometric titration technique to accurately and precisely locate and endpoint (Bark and Bark, 1969). For comparison, a thermometric titration plot of benzoic acid titrated under the same conditions is illustrated in Figure 2.

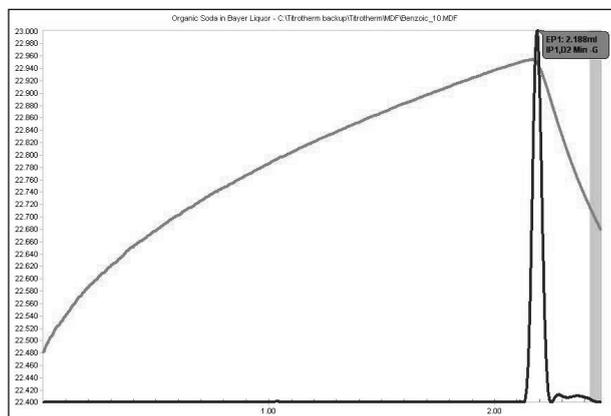


Figure 2. Titration of benzoic acid in propan-2-ol with 0.1 mol/L KOH in propan-2-ol

3. Choice of extractant

Cyclohexanol was chosen as the most suitable solvent as an extractant for the organic species present in the acidified Bayer process liquor after qualitative tests based on the colour of the extract suggested that it was superior to toluene.

Conclusions

A highly reproducible procedure has been developed for the determination of the sodium contribution of acid-extractable organic species in Bayer process liquor.

References

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