

A PROTOTYPE INSTRUMENT FOR THE ELECTROCHEMICAL DETECTION OF SUCROSE CONTAMINATION IN SUGAR REFINERY CONDENSATES - PULSED AMPEROMETRIC SUGAR TRACE ANALYSER (PASTA)

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Abstract

A prototype analyser incorporating commercial analytical instrumentation has been used to monitor the sucrose contamination of boiler feed water. The instrument has been designed to use a commercially available pulsed amperometric detector and incorporates a short chromatographic column. This allows the choice of flow-injection or chromatographic mode of operation. The former is simpler, but non-specific, whereas the latter can be sucrose specific. Results of continuous at-line trials in parallel with total organic carbon (TOC) monitoring are presented.

Keywords: Electrochemical detection; pulsed amperometry; boiler feed water; sucrose carryover.

Introduction

A significant volume of boiler feed water is generated from evaporator condensates in sugar factories and refineries. Efficient steam generation is dependent on the composition of the liquid from which this steam is generated. Sugar industry boiler waters may be contaminated from process liquids entraining sucrose. This sucrose decomposes inside the boiler to form organic acids which lower the pH and increase the rate of corrosion of boiler tubes. These acids need to be neutralised (by caustic addition) and this then further increases the concentration of dissolved solids in the boiler. In high pressure boilers the major source of deposits is from corrosion products. The dissolved solids exacerbate foaming or carryover and organic matter such as sugar tends to 'strengthen' the foam. Water or dissolved solids carried over with the steam can cause damage to engines and turbines. Furthermore, scale or corrosion affects the surface-heating area and reduces the heat flux (Kaiser, 1980; Atherton, 1983). Feed water quality assumes increasing importance with increasing boiler pressure.

The widespread use of high pressure boilers makes it essential that boiler feed water is free of sucrose contamination. This requires an efficient rejection and dumping protocol, which in turn is dependent on detection and fast response to sucrose carryover. Most boiler failures have been attributed to a combination of design faults in the dumping system rather than to the monitoring system. For boiler safety it is better that high levels of sugar contamination are detected with absolute certainty than that traces of carryover are accurately measured. It is important that these high doses are eliminated by an effective sugar monitoring system to protect the boilers.

Various methods have been successfully applied in the raw sugar

factory. These include colorimetric (Parker and Bond, 1958; Bruijn, 1962; Fowler, 1977; Schäffler, 1978), conductometric (Douglas, 1962), pH (Kakuni, 1991), flame photometric (Dale and Lamusse, 1977) or specific ion (Opelka *et al.*, 1975) detection. In the case of stand alone refineries, where ionic impurities are so low that the indirect conductivity measurement is unreliable, total organic carbon (TOC) monitoring has enjoyed some success, in combination with an efficient dumping strategy (Tayfield and Anderson, 1993). The major drawback of TOC monitoring has been the long reaction time (of the order of seven minutes), necessitating the incorporation of large buffer tanks and excessive rejection on occasions. However, with experience, condensate storage and recovery can be optimised. Furthermore, as a consequence of the expense of TOC analysers, condensate streams are frequently combined so that only the composite is analysed.

Pulsed amperometric detection (PAD) has become a widely accepted analytical tool for the measurement of carbohydrates after chromatographic separation (Anon, 1993). This type of detection is reasonably specific for classes of organic compounds. In the initial phase of this project the principle of PAD was tested, but interferences from organic impurities in factory condensates were considered sufficiently troublesome to discontinue the application of PAD to condensate monitoring for sucrose (Reid and Dunsmore, 1991).

Subsequently an in-house cell was manufactured and tested. In an attempt to reduce costs a peristaltic pump (with pulse dampening) was used. Innumerable problems and difficulties were experienced. The cell was extremely difficult to service. The design led to air entrapment, sluggish response, frequent leaks and poor electrical contact. These problems together with the noisy, drifting, pulsing signals obtained caused this approach to be abandoned (Anon, 1997). It was felt that at least a medium pressure pump delivering constant flow was necessary.

In order to assess the suitability of the detection method it was decided that the analytical equipment at our disposal would be used. The investigation reported here is an attempt to examine the feasibility of using PAD to monitor sucrose contamination in refinery condensates.

Method

Principle of pulsed amperometric detection (PAD)

The concept of pulsed amperometric detection is simple. A voltage is applied to a gold electrode where oxidation of carbohydrates (and some other compounds) generates a current. This

current is amplified and can be measured and monitored continuously. Because the oxidation products coat the gold electrode, a pulsed sequence of potentials is used to remove this coating during operation. With the correct selection of this programme manual polishing of the electrode is usually unnecessary (Neuberger and Johnson, 1987b). Although the concept is simple, cell design is important, particularly as regards the relative positioning of the electrodes (Hawkrige, 1984; Kissinger, 1984). Flow-through analytical electrochemical cells are either thin-layer cells or wall-jet cells. Thin layer cells give a high ratio of electrode surface area to solution volume.

Although carbon paste or platinum working electrodes have been used, gold gives higher sensitivity and lower detection limits and is the material of choice for carbohydrates (Neuberger and Johnson, 1987b). The supporting electrolyte (sodium hydroxide solution) provides the high pH necessary for ionisation of the sugars and needs to be free of dissolved oxygen and carbon dioxide. The former leads to baseline disturbances and the latter lowers the reagent pH, causing variable response and the possibility of blockages due to precipitation of sodium carbonate. The presence of surfactants can contribute to electrode fouling and coating.

Cell modification

The indifferent results obtained with the in-house cell coupled with peristaltic pumping were attributed both to the very poor cell design and to the flow variations caused by peristaltic pumping even with pulse dampening. Although Neuberger and Johnson (1987a) used a similar peristaltic pump they indicated

that the detection limit for sucrose was of the order of 360 ng (or about 4 ppm when using 100 μ l of sample) with such pumps. This view is supported by our findings that baseline disturbances from peristaltic pumping limited the sensitivity. Accordingly, a slightly modified commercially available detector was used in conjunction with the analytical equipment described later.

A membrane (Nafion) for isolating the reference electrode from the flowing stream is a component of the analytical cell. This sometimes dries out leading to noisy signals. Because fouling is not an issue with relatively clean condensate streams, this membrane was removed and the electrode well was plugged with teflon tape to reduce the dead volume so created *i.e.* the reference electrode was placed directly in the sample stream. This reduces the frequency of cell servicing. The standard cell gasket was retained (0.014").

Temperature has a significant effect on detector response and it is necessary to thermostat the detector (Schäffler *et al.*, 1996). The same housing served to thermostat the chromatographic column, discussed below.

System design

The system has been designed around a commercially available detector and anion exchange chromatographic column, allowing the choice of flow injection (non specific) or chromatographic (specific for sucrose) operation. Sodium hydroxide (200 mM *i.e.* about 0.8 %) was used as reagent. This was prepared as needed from a 50% stock solution prepared as de-

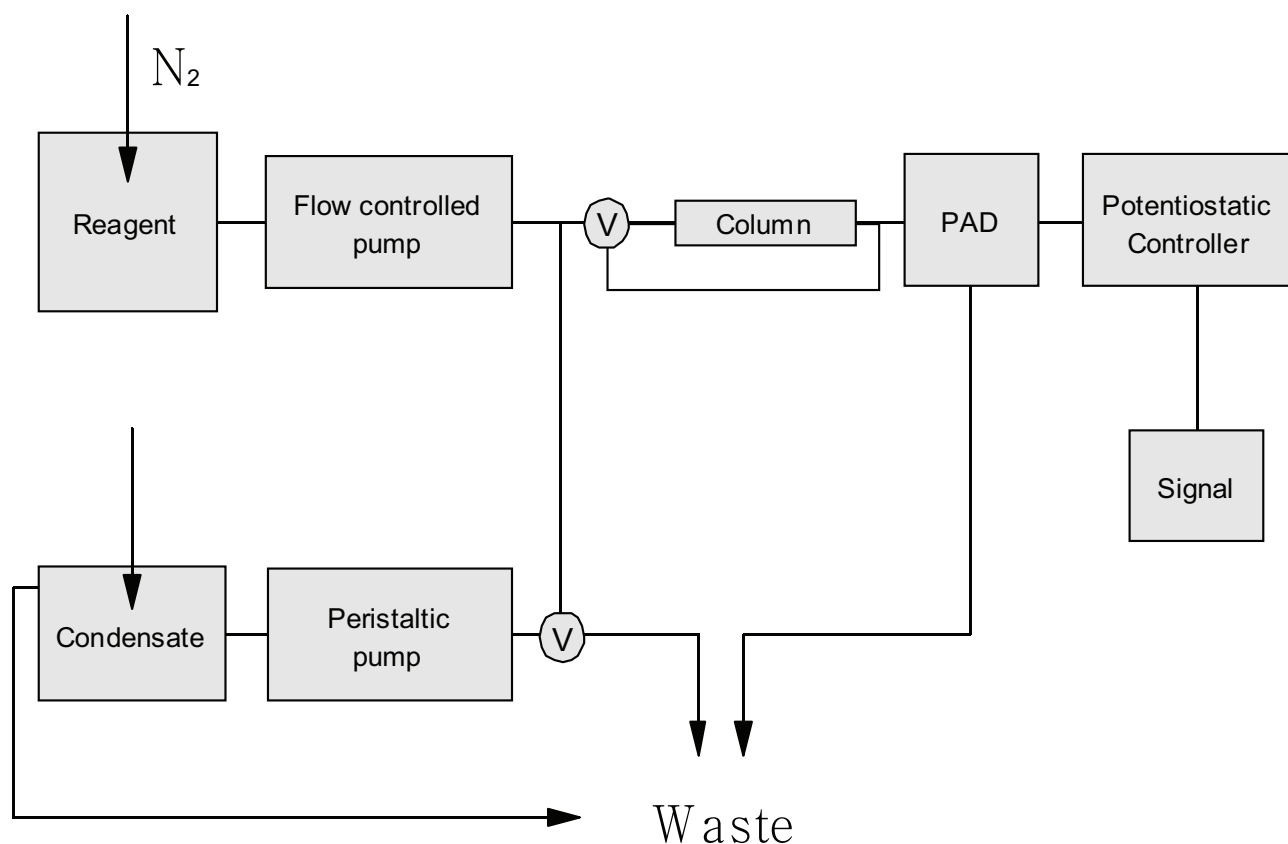


Figure 1. Schematic flow diagram of PASTA instrumentation.

scribed previously (Schäffler *et al.*, 1996). The reagent was sparged continually with nitrogen to remove dissolved oxygen and carbon dioxide. A schematic representation of the instrumental layout is shown in Figure 1.

Equipment and reagents:¹

- (a) HPLC pump, Waters M-45 @ 1 ml/min
- (b) Peristaltic pump, Gilson Minipuls 2 @ 2 ml/min to fill the sample loop
- (c) ESA CouloChem II to control and apply the potential waveform to the cell ($E_1 = 50$ mV; $t_1 = 420$ ms; AD = 220 ms; $E_2 = 750$ mV; $t_2 = 180$ ms; $E_3 = -200$ mV; $t_3 = 360$ ms; Range = 2 or 5 μ A)
- (d) Dionex PAD -2 cell with gold working electrode and 0.014" gasket (Dionex P/N 36276)
- (e) Detector and column housing thermostatted at about 27°C
- (f) SGE LS-3200 autosampler with 6 port Valco A60 valve as sample injector with 100 μ l sample loop
- (g) Rheodyne switching valve to switch stream directly to the detector or via the column
- (h) CarboPac PA1 Guard column (4 x 50 mm) (Dionex P/N 43096)
- (i) HP 3396 integrator and Peak96 to monitor and log the signal
- (j) Reagent, 200 mM NaOH (Analar grade), sparged with nitrogen

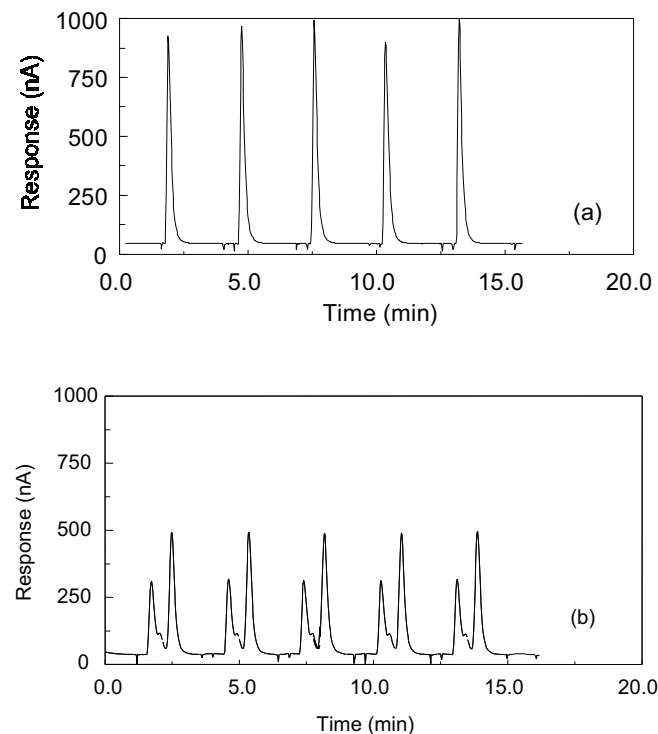


Figure 2. Five sequential injections of refinery condensate with 10 ppm of added sucrose in (a) flow injection mode (single combined peak) and (b) chromatographic column mode (pairs of peaks corresponding to other organic material and sucrose). (100 μ l injections at 2.5 minute intervals).

- (k) Peek tubing (40 thou) was used to connect the components. End or in-line filters (5 μ m) were used on sample and reagent lines.

Results and Discussion

Laboratory trials

Three approaches were considered

- *continuous* sampling, mixing with reagent and monitoring
- *discrete* introduction of short pulses of sample stream into a continuous reagent stream and monitoring. This is known as flow injection (FI) mode
- *discrete* introduction of short pulses of sample stream onto a small chromatographic column before monitoring. This has been designated chromatographic column (CC) mode.

All three approaches were tried. Continuous sampling was found to be unsuitable since the electrode surface tended to foul causing the baseline to drift (Anon, 1996). This was attributed to insufficient recovery time under these conditions. A further disadvantage was the need for two high performance pumps.

With either the FI or CC mode, in addition to a single flow controlled pulse-free pump, only a simple peristaltic pump is needed to keep the sample loop full. A sample size of 100 μ l was selected to avoid significant dilution of the reagent or excessive peak dispersion. A time-controlled valve was used to add this sample to the reagent at defined intervals (*e.g.* every two or three minutes). Performance was good in both the FI (range 5 μ A) and CC (range 2 μ A) modes. Response was linear in the range 0 to 50 mg/l for sucrose, with a 100 μ l injection of 10 ppm sucrose generating 0.45 to 0.50 μ A at peak maximum in the CC mode. Noise was insignificant at a few pA. Analytical residence time was of the order of 45 seconds in the FI mode and about two to three minutes in the CC mode. Typical detector profiles for the two modes of operation are shown in Figure 2. Tests over a period of seven days of continuous operation using a bulk sample of refinery condensate, showed that the system was stable and reliable in either mode. Standardisation using a 10 or 20 ppm sucrose solution was carried out daily.

Refinery trials

The instrument was then run at-line in the Hulref process laboratory in parallel with their current analyser (Aquadoc TOC). Hulref have a sophisticated condensate sampling and dumping protocol in place which includes piping the sample to the laboratory (Tayfield and Anderson, 1993). The sample was taken from the same point as that used for the TOC analyser. Both the TOC and PASTA outputs were datalogged using a PC. Trouble free trials were conducted over a four week period. The PASTA instrument was tested in both the FI and CC modes, whilst the TOC was operated in continuous mode. The installation is shown in Figure 3 and typical results for a sampling period of about nine hours are given in Figure 4. The comparison was favourable.

Although the original request was for a sucrose specific detector, it is clear that other organic impurities may be equally hazardous to high pressure boiler operation, if they degrade to

form corrosive impurities. It has been established that the major component of the background organic load at Hulref is usually ethanol (Tayfield and Anderson, 1993). High background levels have been experienced after prolonged shutdowns and Hulref have learnt to maintain a steady background by slowly 'bleeding in' this contamination which is unlikely to create major problems. With such steady state backgrounds the FI mode (directly comparable to TOC) is the preferred option.

Conclusions

A novel application of pulsed amperometric detection has been demonstrated in a refinery laboratory environment. Favourable comparisons between PAD and TOC monitoring of refinery condensates for organic contamination were obtained. The technique could provide a viable alternative to TOC analysis, but there is a need for the development of ancillary equipment. The possible advantages over TOC include lower residence time, lower capital outlay, less costly maintenance and less costly chemistry, provided that the costly, bulky research instrumentation can be replaced with simpler and possibly cheaper alternatives. The electronics division at the Institute is currently attempting this modification. The system design of-

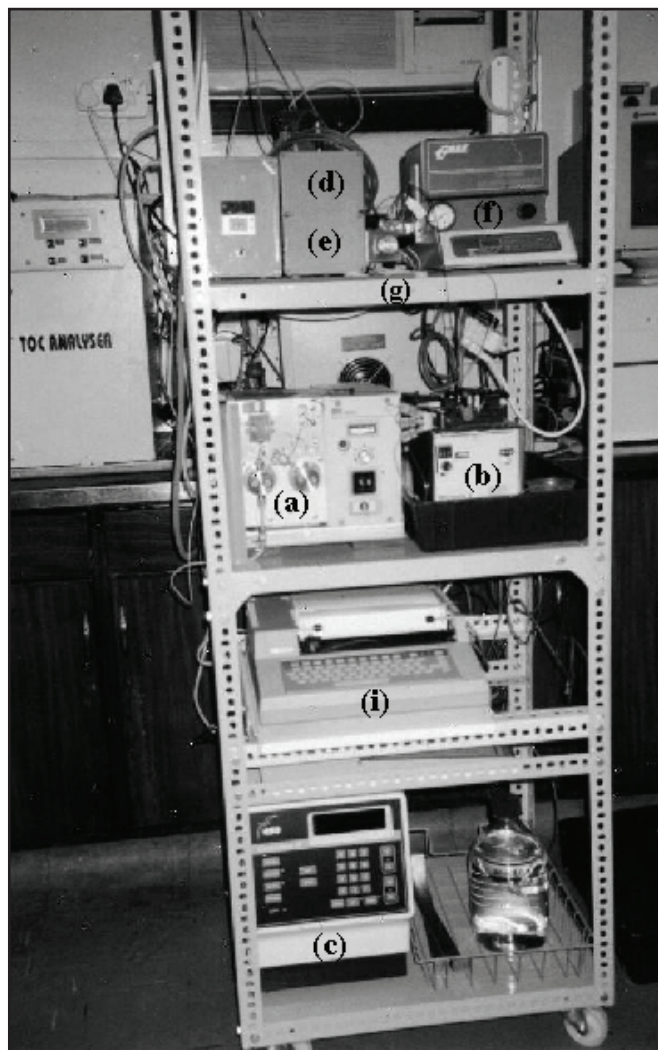


Figure 3. Instrument installed in HulRef process laboratory. Component identification in accordance with that listed under Method.

fers a choice between non specific (organic) and specific (sucrose) operation. For water quality monitoring the FI mode is easier and simpler and probably preferable since total organics are measured. The CC mode is very useful for troubleshooting applications such as pinpointing sucrose leaks.

Sampling, holding tanks and diversion strategies form an integral and important aspect of any monitoring programme and analytical lagtime is often an important constraint - only analytical aspects have been considered here.

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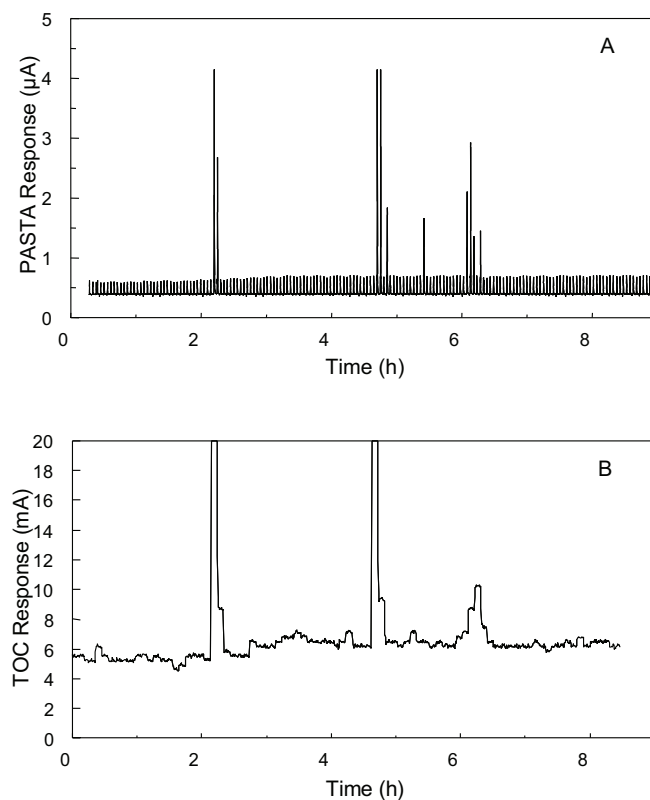


Figure 4. At-line monitoring of refinery condensate - (A) PASTA and (B) TOC.

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¹The mentioning of a tradename or trademark does not infer a preference for a particular product or brand.