Journal of Chromatography, 640 (1993) 303–308
Elsevier Science Publishers B.V., Amsterdam

CHROMSYMP. 2830

The role played by ion chromatography in the assessment of amines for two-phase erosion corrosion control in nuclear electric's steam–water circuits

J. C. Greene* and R. M. Donaldson

Technology Division, Nuclear Electric plc, Timpson Road, Wythenshawe, Manchester M23 9LL (UK)

ABSTRACT

Two-phase erosion corrosion is a world-wide problem and has been experienced in steam-generating plants in both Europe and the USA. In the UK, carbon steel boiler tubes in a number of Magnox Power Stations, operated by Nuclear Electric, have suffered from failures caused by two-phase erosion corrosion. Following a comprehensive investigation of the phenomenon, Nuclear Electric has solved this problem by changing to amine-dosed feedwater in place of the original ammonia treatment. This investigation included laboratory and large-scale rig studies together with a plant trial, which lead to a successful outcome.

This paper describes in detail the important part ion chromatography has played in this project. The analytical procedures are described and calibration curves are included. Examples of practical results obtained in the laboratory, in rig tests and in a plant trial are given. Further examples of cation chromatography will demonstrate application to product purity determination and thermal breakdown behaviour under simulated and real plant conditions.

INTRODUCTION

This paper describes the details of an analytical method for the measurement of amines in aqueous solution based on ion chromatography (IC). The technique was used as part of a major project to investigate a potentially expensive plant problem caused by two-phase erosion corrosion.

Two-phase erosion corrosion is a world-wide problem and has been experienced in steam-generating plants in both Europe and the USA [1,2]. In the UK, carbon steel boiler tubes in a number of Magnox Power Stations operated by Nuclear Electric have suffered failures from this phenomenon. Erosion corrosion occurs when a highly turbulent fluid comes into contact with a mild steel surface interfering with the mechanism of protective oxide film formation by removing soluble iron. It is flow dependent but also solubility dependent and can be retarded by raising the pH of the liquid flowing past the corrosion site. It is also especially prevalent at high steam qualities (*ca.* 70%, w/w) at temperatures of approximately 250°C [3]. Nuclear Electric has considerably reduced this problem by introducing amine-dosed feedwater in place of the original ammonia treatment [4–6].

The study leading to this success was conducted in four successive stages. First, a literature survey identified a large number of possible amines to be considered. The base dissociation constant and the steam–water partition coefficient of each amine were important properties to be considered in judging its suitability. Secondly, laboratory studies were directed at studying the most promising amines. Thirdly, large scale boiler rig investigations tested the effectiveness of a smaller number of the test candidate amines in controlling two-phase erosion corrosion. The boiler rig contains a full scale replication of a singe boiler tube and operates under identical operating conditions of flow, temperature, pressure and heat flux as the plant. Details of the

---

* Corresponding author.

0021-9673/93/$06.00

facility are available elsewhere [4]. Finally, a plant trial lasting two weeks looked at the acceptability of the chosen amine for long term use on the plant. The chosen amine, 2-amino-2-methyl propan-1-ol (AMP), replaced ammonia in the plant in September 1983. More recently, further work has identified an even better amine, 5-aminopentan-1-ol (5-AP), which has been in use in the plant since November 1992 [7]. This paper describes the role played by IC in the last three stages of this major project and concentrates on the analysis of the two amines used in the plant.

AMINE SELECTION

The required amine needed to display a number of key properties in order to be suitable for this special application. It was necessary to achieve a sufficiently high alkaline pH within the boiler at the potential corrosion sites [7]. The amines ability to achieve this is defined by both its base dissociation constant and the steam–water partition coefficient. Additionally, the amine had to be available economically in commercial quantities, to the required purity, be non-toxic and thermally stable up to the maximum boiler operating temperature of 350°C. The selected amine must also be compatible with the circuit materials including the condensate purification plant ion exchange resins [8,9].

EXPERIMENTAL

The two amines in question are water soluble and sufficiently dissociated to produce protonated amine cations and alkaline solutions. Cation-exchange chromatography, with eluent suppression and conductivity detection, was therefore chosen for the analytical chemistry part of this project.

Equipment

A Model 2000i Dionex chromatograph was used in this work. The major components of this system were a high pressure pump, two matched sample loops, columns, a micromembrane eluent suppressor, conductivity cell and meter and an 8-port sample injection valve. A Spectra-Physics Chromjet computing integrator was used for computing the results and the system operation was controlled using an Autoion 100 controller.

Analytical details

Dilute hydrochloric acid, typically 8 m*M*, was used as eluent at a flow-rate of 1.0 ml/min. Sample was injected alternately by means of two matched sample loops. Sufficient sensitivity was obtained with 0.5 ml loops and for the amine concentrations of interest (typically up to 10 ppm) there was no evidence of overloading the separator column. Satisfactory separation was obtained using a cation separating column of the CS2 type. For most applications, the smaller size guard/concentrator (CG2) columns were sufficient to give the necessary separation. Where greater resolution was required, either two CG2 columns were used in series or a CG2 followed by a CS2 was employed. Tetrabutylammonium hydroxide (TBAOH) regenerant (20 m*M*) was used in the micromembrane suppressor at a flow-rate of 2.0 ml/min. The flow-rate was achieved using a peristaltic pump. In earlier work a reservoir fitted with a CO_2 trap was used for the regenerant. For later work, however, an Autoregeneration system was used, leading to lower consumption of the expensive TBAOH. With both systems a background conductivity of less than 1 μS cm^{-1} was obtained consistently.

RESULTS AND DISCUSSION

The level of amine dosed in the plant is in the concentration range 0 to 10 ppm. Multi-level calibrations were, therefore, carried out covering this concentration range. The results of one such calibration for 5-AP are shown in Fig. 1. The calibration using peak area is linear and goes through the origin. In fitting the experimental results to a straight line equation the linear correlation coefficient was 0.9999. Using peak height, the calibration line is curved and when the experimental results are fitted to a straight line equation the linear correlation coefficient is 0.9948. In all the studies reported here, therefore, peak areas were used to determine cation concentrations.

During calibrations, an opportunity was taken to examine the precision of the method. Five successive measurements were made of a 5.0-ppm standard of AMP. A standard deviation equivalent to 0.003 ppm of AMP was obtained from these results. Further results obtained from 5-AP are given in Table I. The results show that the method is capable of

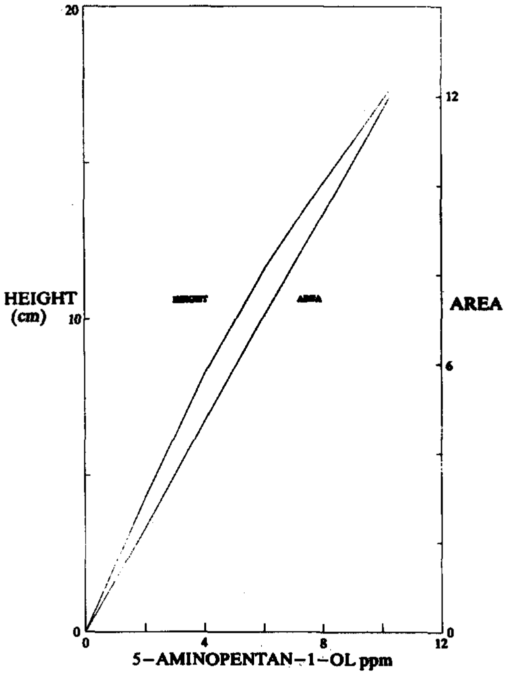

Fig. 1. Calibration for 5-aminopentan-1-ol using peak area and peak height.

good precision. The good chromatographic peak profiles together with the steady baselines obtained by the method contribute significantly to this good reproducibility.

When an analytical method is used continuously it is important to establish the required frequency of calibration. This information can be deduced from the long-term performance of the method obtained during the full scale boiler rig tests. The system was standardised with 0.5 ppm AMP and 0.58 ppm 5-AP prepared from stock 1000 ppm standards at the beginning of the test and the method was run continuously day and night. Standardisations were repeated after four and nine days with freshly prepared standards each time. The fresh 0.5 ppm AMP gave values of 0.480 ppm and 0.472 ppm, based on the original response factor, after four and nine days respectively. The corresponding values for the 5-AP were 0.568 ppm and 0.553 ppm. The causes of this gradual loss in sensitivity were not explored. One possible explanation may lie in the performance of the Autoregeneration system such that the background conductivity may rise slowly leading to a slight change in sensitivity. Nevertheless, it is clear that for the method described, it is appropriate to recalibrate the analytical system at intervals of approximately every two days.

TABLE I

METHOD STATISTICS

Amine	Concentration (ppm)	Standard deviation (ppm)	Number of measurements
AMP	0.50	±0.003	5
5-AP	0.58	±0.003	5
5-AP	0.19	±0.0026	7

In the laboratory studies several amines were investigated and all of these amines were quantified by the IC method described. An example of the determination of ammonia, AMP and 5-AP is shown in Fig. 2. The concentrations of ammonia, AMP

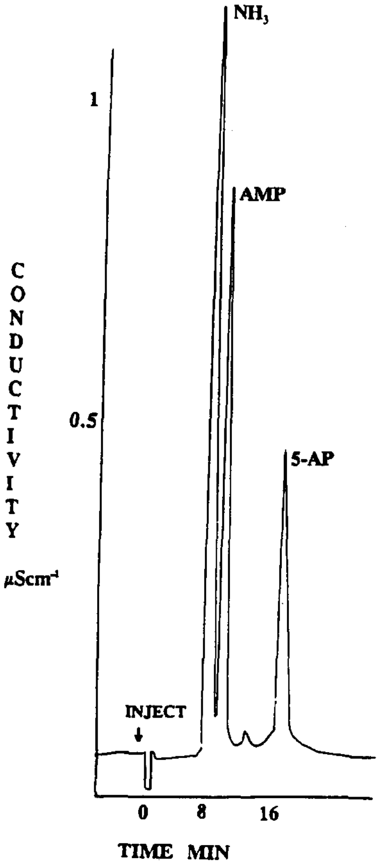

Fig. 2. Separation of ammonia, AMP and 5-AP.

and 5-AP in this example are 0.2, 0.5 and 0.5 ppm respectively. The small peak detected after the AMP has been identified as 2-aminobutan-1-ol. This compound is an impurity found in the AMP and is present in the supplied product at a concentration of approximately 3%. This example demonstrates the ability of the IC method in assess product purity.

The high temperature studies in the laboratory included measurements of the amine dissociation constant, the steam–water partition coefficient and thermal stability. Following these, the most promising candidates were selected to go forward for further evaluation on a large scale boiler rig facility. As described earlier, the boiler rig contains a full scale replication of a singe boiler tube and operates under identical operating conditions of flow, temperature, pressure and heat flux as the plant. The chromatograms shown in Fig. 3 were obtained during the four week full scale boiler rig trial. At the test section inlet, 0.5 ppm AMP was detected together with the trace of 2-aminobutan-1-ol but there was an absence of ammonia. On passing through the heated test section and flowing around the circuit to the polishing plant the fluid is diluted with pure make-up water by approximately 5%. On the basis of this dilution effect, the measured concentration of AMP at the polishing plant inlet would be expected to be 0.475 ppm. The measured concentration was 0.46 ppm AMP and this provides evidence of thermal degradation of AMP in the heated test section. The simultaneous formation of ammonia as one of the breakdown products of AMP is further evidence of this. Although the IC technique was being used primarily to quantify the amine concentration it can be seen that it is sufficiently versatile to simultaneously detect and quantify the ammonia.

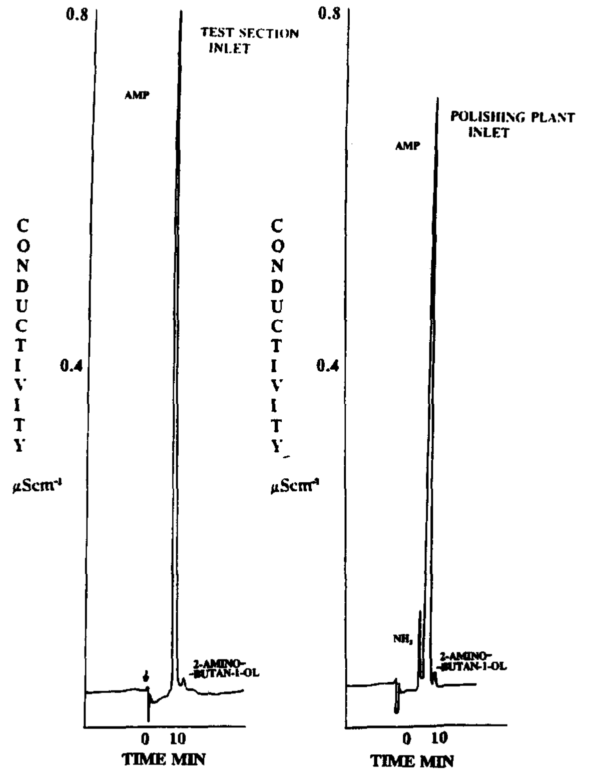

Fig. 3. Measurements of AMP during full-scale rig studies showing thermal breakdown.

Results obtained during the plant trials are shown in Fig. 4. These chromatograms were obtained when amine dosing was changed from AMP to 5-AP during the two week trial. There is good resolution between AMP and 5-AP as shown in Table II.

Further plant measurements were carried out to explore the thermal stability characteristics of the 5-AP (Fig. 5). These chromatograms of boiler inlet and steam, obtained during the 5-AP plant trial, demonstrate the stability of 5-AP. Despite a boiler inlet temperature of 130°C and boiler outlet steam temperature of 350°C and an overall residence time of approximately 5 min, no thermal breakdown products were detected. Boiler inlet and steam concentrations were identical at 6.2 ppm 5-AP.

In normal plant operation the feedwater dosing requirements are controlled and monitored continuously by direct specific conductivity measurement.

TABLE II

RESOLUTION BETWEEN AMP AND 5-AP CHANGE-OVER

Time since change-over (h)	AMP (ppm)	5-AP (ppm)
0	7	0
1	2.5	3.5
2	1	4
4	0.8	7
5	0.6	8

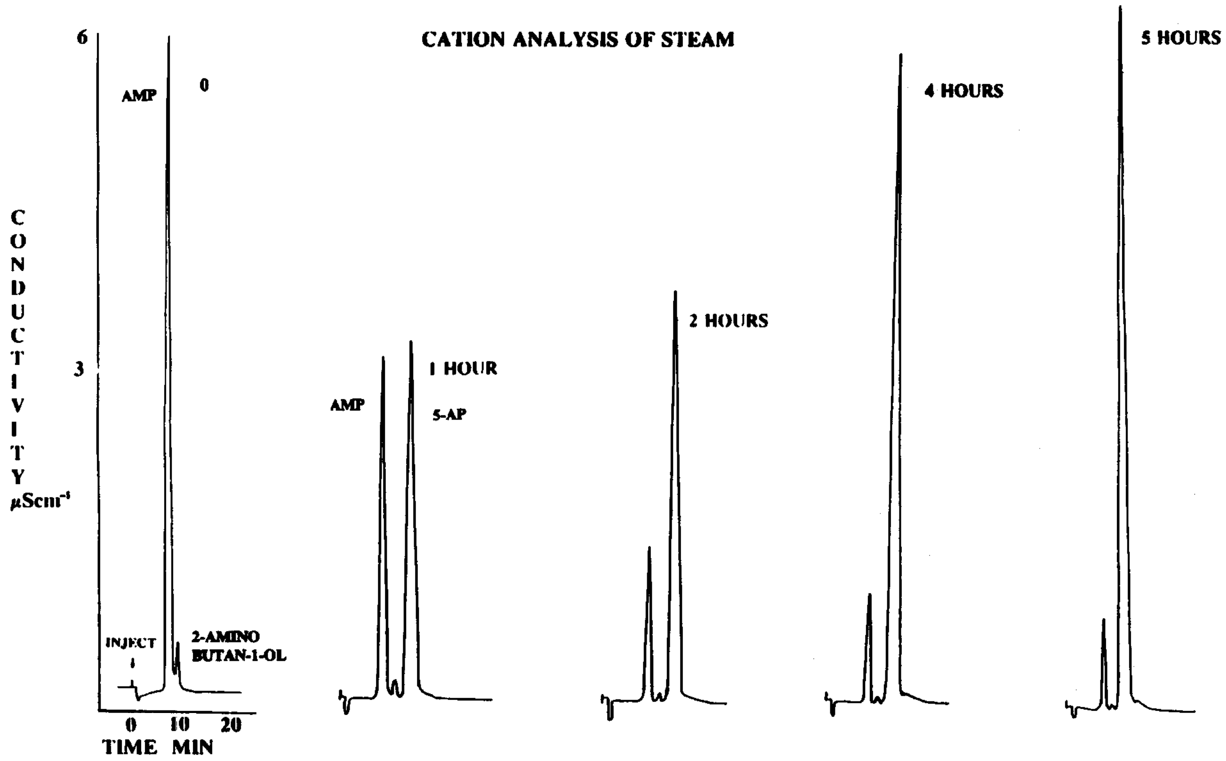

Fig. 4. Measurements taken during plant trial during change-over from AMP to 5-AP.

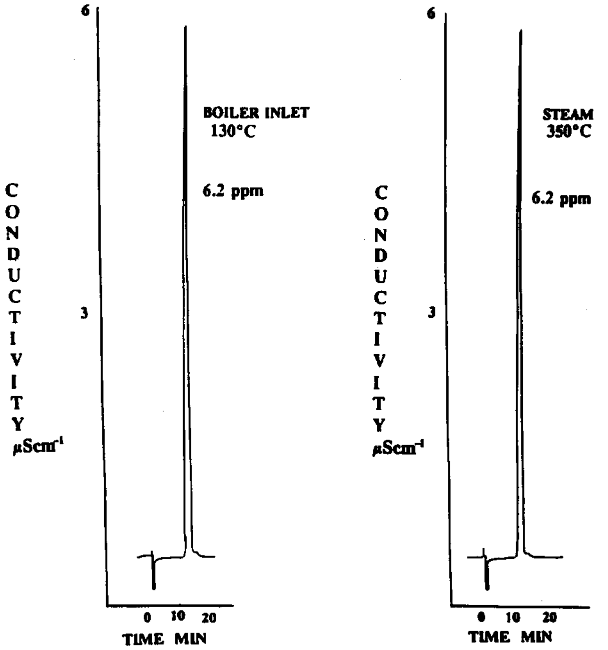

Fig. 5. Measurements made during plant trial of 5-AP to assess thermal stability (residence time *ca.* 5 min).

Experience has shown that this method is robust and reliable. Regular double-checks are made using a separate, independent analytical procedure. Prior to the adoption of continuous AMP dosing in the plan it was necessary to produce a plot relating amine concentration to specific conductivity. One such curve is shown in Fig. 6. This was produced

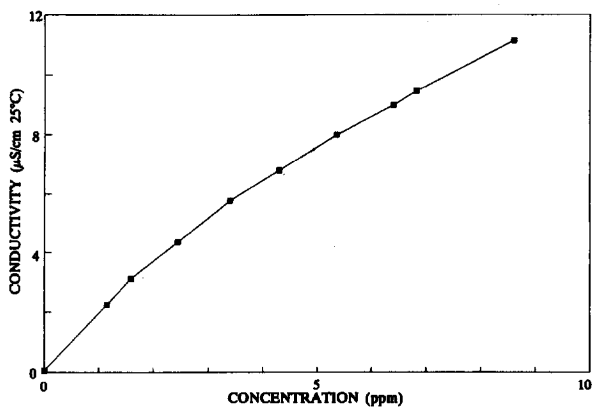

Fig. 6. Relationship between conductivity and concentration of AMP for use in continuous plant monitoring.

during boiler rig trials by dosing AMP into the ultra pure recirculating water at different dosing rates. Samples were drawn continuously, thermostatted to 25°C, through a sensitive, calibrated conductivity cell. Samples from the cell outlet were analysed by IC. More recently, a similar relationship has been established for 5-AP. These curves have been used by plant operators for routine continuous plant monitoring purposes.

CONCLUSIONS

From the foregoing description of the analytical method, it is apparent that it has played a vital role in a successful project. It is suitable for analysing a wide range of water soluble amines. The method has been shown to be sensitive and specific. Tests have been described which measured the precision of the method applied to two amines at two different concentrations. Examples have been given showing its application to the determination of multicomponent mixtures. Its full versatility was displayed in the analysis of amines covering the varied environments of the laboratory, large scale rig and power station plant. The required sensitivity and precision were achieved because of the well resolved peaks and low conductivity, stable baseline. Capable of identifying and quantifying a multicomponent cation mixture in one analysis in about 20 min, the technique was applied to product purity evaluation and thermal stability studies. The long-term performance of the method, extending over 216 h, was demonstrated in the full scale boiler rig studies and from this the calibration frequency requirements were determined.

ACKNOWLEDGEMENTS

This paper is published by permission of the Director of Technology, Nuclear Electric plc. The authors wish to acknowledge the technical contributions of their colleagues within the Company.

REFERENCES

1 C. F. Palomero and K. Garbett, *Workshop on Use of Amines in Conditioning Steam/Water Circuits, Tampa FL*, EPRI, 1991, Paper No. 34.

2 C. F. Palermo, E. Pla and K. Garbett, *BNES Conference on Water Chemistry of Nuclear Reactor Systems 3*, 1983, Vol. 1, pp. 235–242.

3 M. J. Fountain, G. S. Harrison, D. Penfold, J. C. Greene and M. A. Walker, *Proceedings of the 45th International Water Conference, Pittsburgh, PA*, 1984, pp. 393–399.

4 D. Penfold, G. S. Harrison, J. C. Greene and M. A. Walker, *BNES Conference on Water Chemistry of Nuclear Reactor Systems 4*, 1986, Vol. 1, pp. 347–353.

5 M. R. Darvill, A. J. Bates, J. C. Bates, D. J. Gardner and M. A. Sadler, *BNES Conference on Water Chemistry of Nuclear Reactor Systems 4*, 1986, Vol. 2, pp. 175–182.

6 M. J. Fountain, E. A. M. Wetton and G. G. Lewis, *Workshop on Use of Amines in Conditioning Steam/Water Circuits, Tampa, FL*, EPRI, 1991, Paper No. 33.

7 E. A. M. Wetton and G. G. Lewis, *BNES Conference on Water Chemistry of Nuclear Reactor Systems 4*, 1986, Vol. 1, pp. 355–361.

8 R. R. Harries, J. C. Bates and J. C. Greene, *BNES Conference on Water Chemistry of Nuclear Reactor Systems 5*, 1989, Vol. 1, pp. 247–255.

9 M. J. Fountain, J. C. Greene and M. G. Jones, *Workshop on Use of Amines in Conditioning Steam/Water Circuits, Tampa, FL*, EPRI, 1991, Paper No. 39.