Thermochimica Acta, 237 (1994) 295–304
Elsevier Science B.V., Amsterdam
SSDI 0040-6031(93)01662-M

The determination of quartz using differential scanning calorimetry

G.A. Norton

Ames Laboratory, Iowa State University, Ames, IA 50011, USA

(Received 13 September 1993; accepted 6 December 1993)

Abstract

Based on the results of this feasibility study, differential scanning calorimetry appears to be a promising technique for determining quartz in powdered samples. The method can avoid interferences, uses relatively inexpensive equipment compared to many of the more conventional techniques, and requires minimal operator skill. For samples containing quartz only, the method has good precision and sensitivity and exhibits a linear response for a wide range (20–10 000 μg) of quartz contents. Although as little as 20 μg of quartz could be detected, the lower limit of detection was not determined. Also, estimates of accuracy and precision for quartz in sample mixtures are still needed. It is likely that optimization of instrumental and sample mounting parameters will result in improved peak response, detection limits, and precision.

INTRODUCTION

Quartz (SiO_2) is commonly determined in environmental and geological samples. Analytical methods such as X-ray diffraction (XRD), infrared (IR), and colorimetric techniques are commonly employed for this purpose. Although those methods generally have good sensitivity and precision, some of the sample preparation procedures are complex or time consuming, and analyses are complicated by inherent analytical difficulties. For example, preferred crystal orientation, matrix effects, and mineral interferences can adversely affect analyses by XRD. The IR method is also affected by mineral interferences, while the colorimetric method is tedious and susceptible to errors due to quartz losses or retention of silicates during sample digestion.

A thermoanalytical technique known as differential scanning calorimetry (DSC) is a potential alternative for determining quartz which offers a number of advantages over the more conventional methods, including easy avoidance of interferences, less costly equipment requirements, and ease of sample preparation. DSC is similar to another thermoanalytical technique, differential thermal analysis (DTA). Although DTA has been used to determine quartz in geological samples, little or no information is available in the literature on the use of DSC for that application. Because DSC has a number of advantages relative to DTA, preliminary tests were performed in this study to determine the feasibility of using DSC for the quantitative determination of α-quartz.

BACKGROUND

DTA and DSC have been used for diverse chemical and mineralogical applications [1]. Quartz can be determined by those techniques by monitoring the rapid and reversible endothermic inversion which occurs at about 573°C as the quartz converts from α-SiO_2 to β-SiO_2 during heating. Conversely, an exothermic $\beta-\alpha$ inversion is observed upon cooling. In one study, analyses of about 250 natural quartz samples indicated that the inversion temperature varied by only 2.5°C or less for over 95% of the samples examined [2]. The magnitude of the peak associated with this inversion is proportional to the amount of quartz present. The inversion is weak because the crystals undergo a displacement and rotation rather than a disruption of linkages in the SiO_4 tetrahedra [3]. However, it can be easily detected using sensitive thermoanalytical techniques. Mineral interferences can be avoided by using the cooling curve or by using the heating curve for a sample which has already been heated through the temperature range containing the $\alpha-\beta$ inversion. Those approaches avoid interferences since the inversion is reversible, while other sample changes in the temperature region of interest are not.

In DTA, endothermic and exothermic events in the sample are recorded by plotting the temperature difference between the sample and a thermally inert reference material as the temperature is increased at a constant rate. DSC, by contrast, measures the amount of energy (supplied to either the sample or reference material) necessary to keep the sample and reference material at the same temperature. DSC is preferred to DTA for quantitative work since DSC is more direct and requires fewer calibration steps [4]. Also, whereas samples for DTA analysis are loosely mounted in open sample cups, samples for DSC analysis are mounted in covered pans and then compacted and crimped in a sample press. Compacting the sample reduces possible effects from sample packing and thermal conductivity variables.

Although little or no data on determining quartz by DSC has appeared in the literature, some pertinent information exists in whcih DTA was used to examine quartz. In one study, DTA had better precision than XRD in the determination of quartz in a variety of geological samples [5]. In another study, a calibration curve with a precision of about ±1% (absolute) was obtained for mixtures of quartz (minimum of 10 wt%) and alumina [6]. In that work, no significant variations in peak height were observed for quartz samples from different localities. Although there have been some anomalies in which DTA gave substantially lower results for quartz than expected based on the total silica content, this is probably due to the presence of non-quartz silica in the samples [6].

For samples prepared in the laboratory, the intensity of the 573°C quartz inversion observed by DTA typically decreases with decreasing particle size as the respirable size range is approached. This is particularly relevant in environmental applications, such as estimating worker exposure to quartz in respirable dusts. Results from one study suggested that changes in thermal conductivity were responsible for this phenomenon [7]. However, it is generally believed that the decreased thermal response for finely-ground samples is due to the production of an amorphous silica surface layer during fine grinding rather than from a change in heat transfer conditions. In one study, the thermal responses could be restored to their original values by etching the samples with HF to remove the non-quartz layer [8]. Because pulverizing quartz results in a layer of amorphous silica, α-quartz standards are not identical [9]. However, this does not preclude determining quartz by DTA or DSC if the proper standards are used, since the true quartz content is being measured. In this regard, extra care must be taken to ensure that the crystalline α-quartz content of the standards is known.

In some studies, smaller peaks were observed by DTA for chalcedony (a very fine-grained form of quartz) than for macrocrystalline quartz [10, 11]. Thus, DTA may give low results if chalcedony is present. However, sample grinding procedures were not discussed. This is an important consideration since fine grinding appears to produce a surface layer of noncrystalline silica that is not detected by DTA.

Because there is evidence that quartz may be "lost" by reacting with calcite ($CaCO_3$) to form wollastonite ($CaSiO_3$) during heating, various researchers have studied that possible reaction. In one study, DTA curves did not show any evidence of wollastonite when quartz was heated with $CaCO_3$, but a small exothermic peak which might be due to the presence of wollastonite was observed when precipitated SiO_2 was used [10]. Based on those results, reactions of calcium with silica to form wollastonite were deemed unlikely, although it was believed that wollastonite could possibly form if the silica is very finely divided and dispersed. Similar experiments with iron and magnesium compounds showed no evidence of the formation of iron or magnesium silicates. However, NIOSH states that a loss of quartz will occur if calcite is present and samples are ashed in a muffle furnace, necessitating prior extraction of the calcite with HCl [12]. Additional studies in this area are required.

DTA is considered to be a reliable method for measuring the true α-quartz content of a sample and is an established technique for quantitative work [11]. However, as mentioned previously, there are a number of advantages of using DSC rather than DTA for quantitative analyses. In addition, there have been major improvements in thermoanalytical instrumentation and analysis software since the DTA studies discussed above were performed.

EXPERIMENTAL

Samples

The α-quartz used in this study was from the St. Peter sandstone formation ($\geqslant$98% SiO_2) in Iowa. Four nominal size fractions of quartz were prepared. These were, (1) plus 200 mesh to minus 100 mesh (75–150 μm), (2) plus 325 mesh to minus 200 mesh (45–75 μm), (3) minus 325 mesh (less than 45 μm), and (4) minus 10 μm. Except for the minus 10 μm fraction, the quartz was pulverized manually in a porcelain mortar and pestle and sieved using ASTM standard sieves. Separate aliquots of the original sample were used for each size fraction. The nominal minus 10 μm sample was prepared by grinding a quartz slurry in a motorized Brinkman model RM-O mortar grinder using a sintered corundum mortar and pestle. After grinding, the slurry was passed through a 10 μm filter bag and the quartz suspension passing through the filter bag was filtered on Gelman GN-6 (0.45 μm) membrane filters using a Gelman magnetic filter funnel. The quartz collected on the Gelman filters constituted the minus 10 μm fraction. To check the particle size of this sample, particle size analyses were performed with a Leeds and Northrup Microtrac particle size analyzer and by examining photomicrographs obtained with a Jeol 840A scanning electron microscope. The analyses indicated that the nominal minus 10 μm sample was at least 75% minus 10 μm and at least 50% minus 5 μm. Except for the studies on particle size effects, the 45–75 μm fraction was used for all the tests in this study.

In addition to the above samples containing SiO_2 only, two sample mixtures were prepared. One mixture consisted of 25% (wt) each of quartz, pyrite, illite, and kaolinite. That sample was used to demonstrate the elimination of potential interferences during initial heating of the sample. The second mixture consisted of 5% (wt) quartz and 95% Al_2O_3 and was used to acquire information on potential detection limits in sample mixtures.

Thermal analysis

Samples were analyzed by DSC using a Du Pont model 2000 thermal analysis system and a model 2910 differential scanning calorimeter. Temperature calibrations were performed using the $\alpha-\beta$ inversion of quartz, which was assumed to be at 573.0°C. The cell constant was determined by using zinc for enthalpy of fusion calibrations. The nature of the experiments did not require implementation of more stringent calibration procedures. Samples were weighed directly into tared 6 mm diameter aluminum pans, covered with an aluminum lid, and crimped with a Du Pont sample encapsulating press. For sample quantities of less than 0.5 mg, a Perkin-Elmer AD-6 autobalance was used. All other samples were weighed using a Mettler AE100 electronic analytical balance. Both balances were calibrated prior to use.

Samples were analyzed by DSC by heating to 600°C at a rate of 20°C min^{-1}. An empty aluminum pan with a crimped lid was used as the reference sample. The endothermic transition of α-quartz to β-quartz at about 573°C was measured. Peak areas were integrated using instrument software packages to obtain the total enthalpy change in millijoules. Peak temperatures and extrapolated onset temperatures were also recorded.

RESULTS

A typical DSC heating curve showing the α–β inversion for a 10 mg sample of pure quartz is shown in Fig. 1. As can be seen, the peak associated with this inversion is very sharp due to the rapid nature of the physical alteration within the sample. The slight change in the baseline location after the peak is due to a change in the heat capacity of the sample resulting from the crystal reorientation.

In Fig. 2, DSC curves for a sample mixture containing quartz, pyrite (FeS_2), and clays are shown. The advantage of preheating the sample to avoid mineral interferences is evident. Potentially interfering thermal events

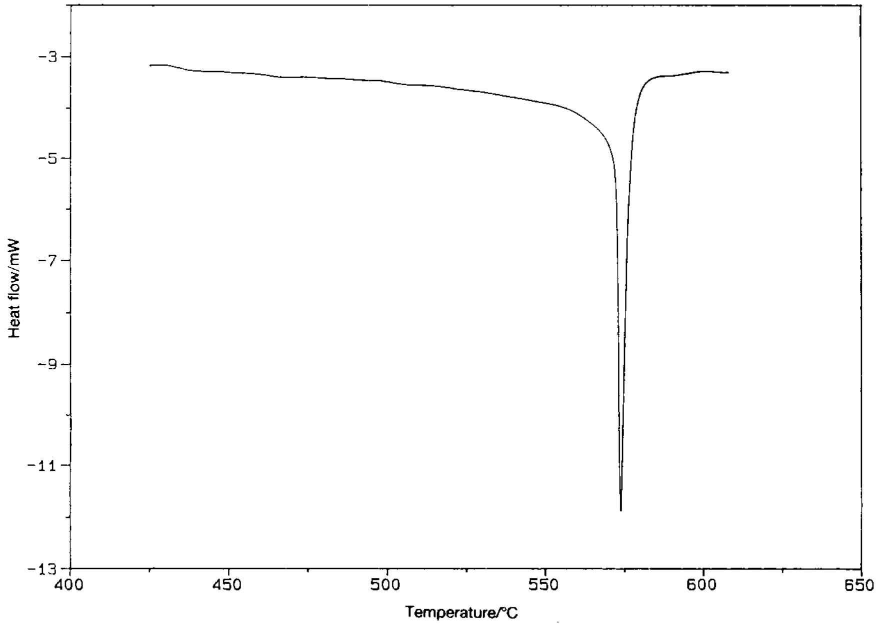

Fig. 1. DSC curve for a 10 mg sample of quartz.

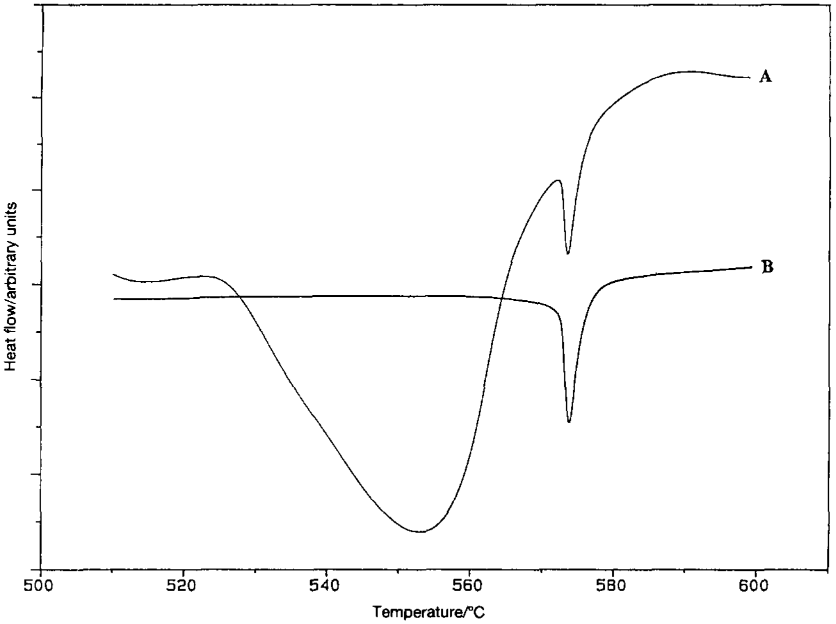

Fig. 2. DSC curves for a mixture of quartz, pyrite and clays during initial heating (curve A) and reheating of the mixture (curve B).

are clearly present in the initial heating curve (curve A), but are absent when the sample was heated for a second time (curve B). Alternatively, the exothermic inversion in the cooling curve could have been used to avoid the interferences. The quartz peak at about 573°C is slightly larger in curve B than in curve A. This is probably due to a decrease in sample mass (and, therefore, higher quartz concentration) after heating because of dehydration of the clays and destruction of the pyrite.

Results of the tests on sensitivity, linearity of calibration curves, and particle size effects are discussed individually below.

Effects of sample quantity

For these tests, sample quantities of 20, 48, 99, 220, 396, and 10 000 μg of quartz ($\geqslant$98% purity) were used with no added minerals. Plots of sample quantity versus peak area (in mJ) were obtained. The thermal response (i.e. changes in peak area) was linear over the entire range of sample quantities, which is favorable from an analytical standpoint. The linear curves suggest that thermal diffusion variables do not pose significant analytical problems for samples containing only quartz. The DSC curves for the 99 and 20 μg samples are shown in Figs. 3 and 4, respectively, to demonstrate typical signal-to-noise ratios for those sample quantities under the experimental conditions used. The fact that as little as 20 μg quartz was detected

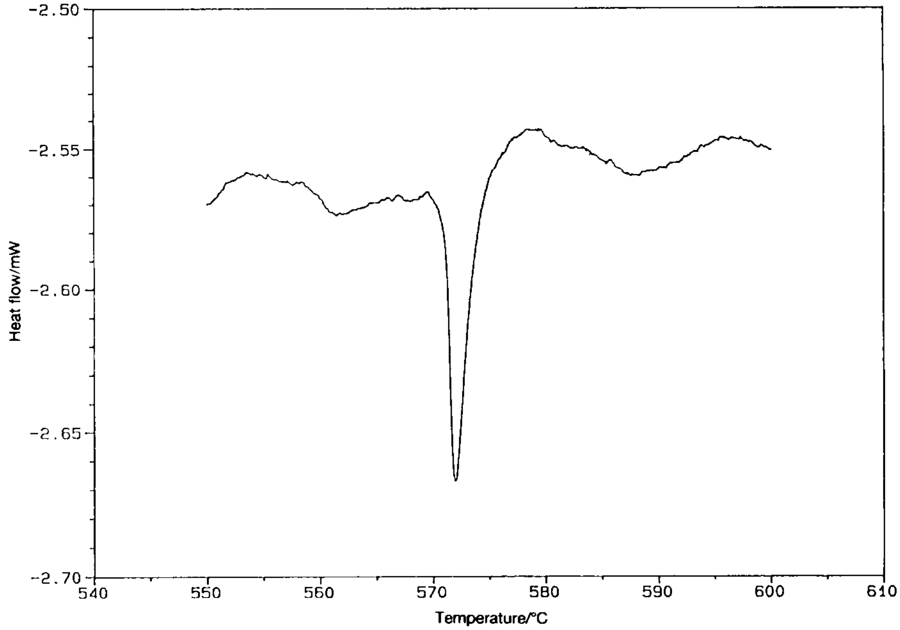

Fig. 3. DSC curve for a 99 μg sample of quartz.

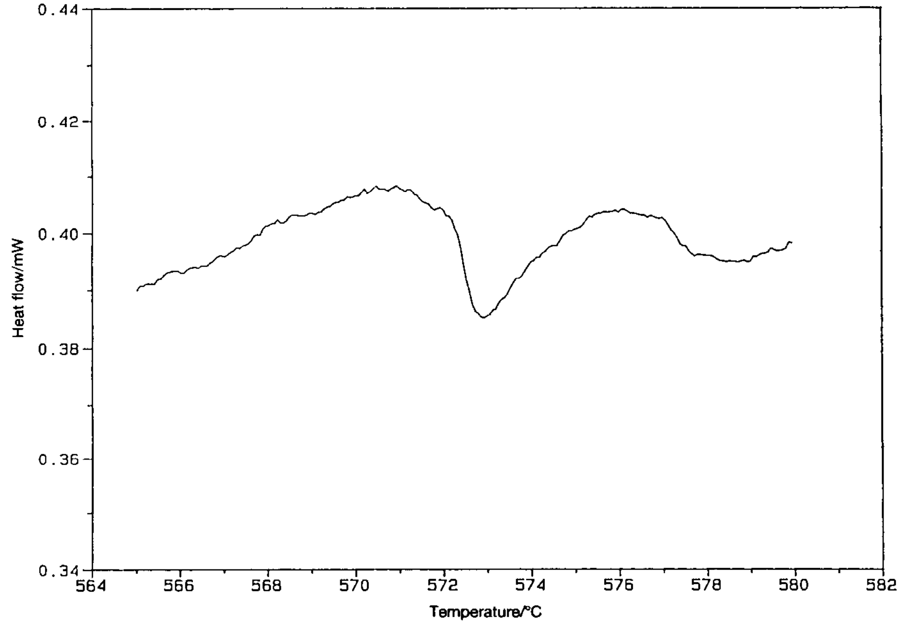

Fig. 4. DSC curve for a 20 μg sample of quartz.

demonstrates that the method has good sensitivity. However, this does not necessarily constitute the lower limit of detection. This is the minimum sample quantity used, and smaller sample quantities may still have been detectable using the same analysis conditions. Also, thermal response may be significantly improved after instrumental and sample mounting parameters have been optimized.

The heating rate is one of the most important instrumental variables. Increasing the heating rate will generally result in more prominent peaks, but may result in decreased precision. Although peak heights tend to increase when faster heating rates are used, the peak areas may not be significantly affected. If the latter is true, the heating rate used to obtain the calibration curve may not need to match the one used when analyzing actual samples.

Effects of particle size

With the exception of the minus 10 μm fraction, there was no significant (less than 3% relative) decrease in peak area as particle size decreased when the sample quantity used for these tests (10 mg) remained constant. For the minus 10 μm fraction, the peak area was about 15% lower than that of the other size fractions. This observation corroborates results of studies by other researchers who used DTA rather than DSC. If the decreased thermal response for the minus 10 μm fraction is due to the presence of non-quartz silica, as suggested by data in the literature, this clearly demonstrates the need for ensuring that the true α-quartz content of the standards is known.

Effects of sample concentration

For the sample which consisted of 5.0% quartz in Al_2O_3, an excellent peak with an area of 1.7 mJ was obtained (see Fig. 5). Using the total sample mass (5.4 mg) and the plots of sample quantity versus peak area (in mJ), a quartz concentration of 4.8% was calculated. This is in excellent agreement with the theoretical value of 5.0%, particularly in view of the fact that instrumental and sample mounting parameters have not been optimized. Also, sample inhomogeneity is a factor which must be considered. Based on these results, it appears that DSC may be able to detect 1% quartz or less in some mixtures. However, the detection limits should be determined in a variety of matrices to ensure that thermal diffusion parameters or other factors do not result in analytical difficulties.

Precision

Depending on where peak limits were chosen for DSC curves from samples containing only quartz, peak areas varied by up to 15% (relative)

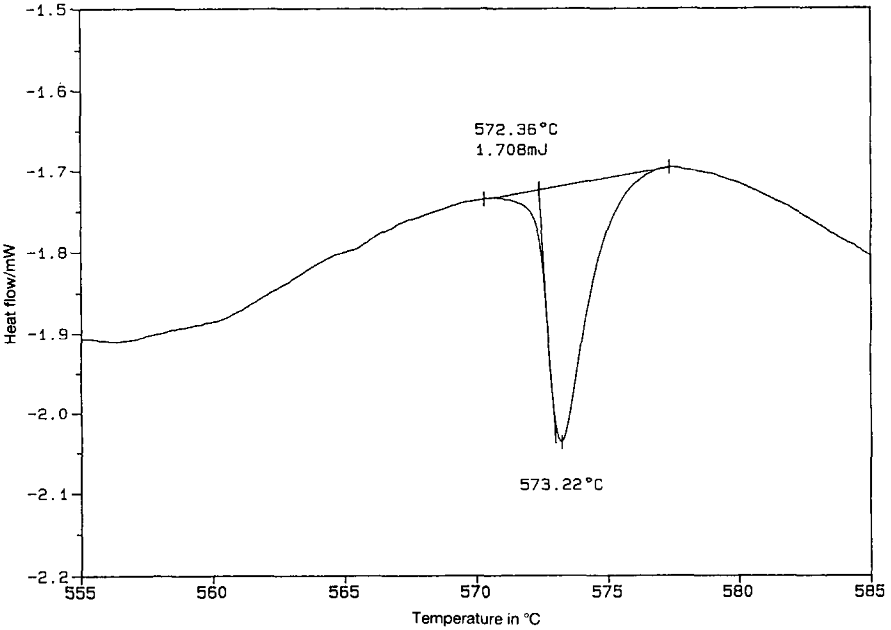

Fig. 5. DSC curve for a mixture containing 5% quartz and 95% Al_2O_3 by weight.

for the 48 μg sample, but varied by less than 2% (relative) for the 99 μg sample. This is due to the fact that the peak boundaries at the larger sample quantities were more clearly defined. When the 20 μg and 99 μg samples were rerun, peak areas were within 10% of those from the corresponding peaks for the previous runs. When the 396 μg sample was rerun, the peak area was within 1% of that which was obtained previously. It is likely that precision can be improved substantially by modifying instrumental and data analysis procedures.

For samples that were rerun (as opposed to reanalyzing a given DSC curve), the peak temperatures were reproducible to within 1°C or better. Between samples, peak temperatures ranged from 572 to 574°C.

CONCLUSIONS

The DSC method appears to have a great deal of potential for determining α-quartz in powdered samples. The determination can be performed in 30 min or less and requires no operator time during that period. The time requirements can be reduced substantially by heating the sample as fast as possible to 500°C and then decreasing and stabilizing the heating rate for analyzing the temperature region of interest. The technique is sensitive, has good precision, can avoid interferences, uses relatively inexpensive equipment, and requires minimal operator skill. Also, acids or other chemicals are not required.

It is likely that optimization of instrumental, sample mounting, and data analysis parameters will result in improved detection limits and precision. Although this work constituted an exploratory study, the precision and sensitivity of the DSC method appear to be approximately comparable to those of commonly used methodologies based on results obtained thus far.

ACKNOWLEDGMENTS

I thank Rachel Peters and Bob Dawson for their help in preparing the quartz samples, Jim Pollard for performing the Microtrac analysis, and Warren Straszheim for performing the SEM analysis. This work was supported by the Iowa State Mining and Mineral Resources Research Institute through the Department of the Interior's Mineral Institutes program administered by the U.S. Bureau of Mines under Allotment Grant No. G1114119.

REFERENCES

1 W.W. Wendlandt, Thermal Analysis, 3rd Edn. John Wiley, New York, 1986, pp. 359–460.
2 M.L. Keith and O.F. Tuttle, Am. J. Sci., Bowen Vol., Part 1, (1952) 203.
3 B. Mason and L.G. Berry, Elements of Mineralogy, W.H. Freeman, San Francisco, 1968, pp. 406–409.
4 J.W. Dodd and K.H. Tonge, Thermal Methods, John Wiley, New York, 1987, p. 142.
5 J.B. Rowse and W.B. Jepson, J. Thermal Anal., 4 (1972) 169.
6 R.W. Grimshaw and A.L. Roberts, in R.C. Mackenzie (Ed.), The Differential Thermal Investigation of Clays, London Mineralogical Society, London, 1957, pp. 275–298.
7 B. Weiss, E.A. Boettner and M. Stenning, Arch. Environ. Health, 20 (1970) 37.
8 P.B. Dempster and P.D. Ritchie, J. Appl. Chem., 3 (1953) 182.
9 J.W. Edmonds, W.W. Henslee and R.E. Guerra, Anal. Chem., 49 (1977) 2196.
10 S.St.J. Warne, J. Inst. Fuel, 38 (1965) 207.
11 S.St.J. Warne, J. Inst. Fuel, 43 (1970) 240.
12 NIOSH Method 7500, NIOSH Manual of Analytical Methods, Received from the Department of Health and Human Services, Centers for Disease Control, NIOSH, Cincinnati, OH, revised 15 May 1989.