JOURNAL OF MATERIALS SCIENCE 14 (1979) 1370–1374

Direct analysis of solid cadmium mercury telluride by flameless atomic absorption using interactive computer processing

F. GRAINGER, I. G. GALE
Philips Research Laboratories, Redhill, Surrey, UK

This paper describes a solid sampling technique for the quantitative measurement of impurities in cadmium mercury telluride (CMT) in the ppb region. It has been used to calibrate the spark source mass spectrograph (A.E.I. MS7) analysis of this material. Typical detection limits obtained are: 0.0002 ppmw Ag, 0.002 ppmw Cu, 0.001 ppmw Fe, 0.0002 ppmw Mn, 0.002 ppmw Cr, 0.004 ppmw Al, 0.0001 ppmw Na, 0.000 06 ppmw Mg, 0.01 ppmw Si. The solid sample is directly analysed by flameless atomic absorption and the method is shown to give results precise to about 10%. Aqueous standards are used throughout and area measurements are found to be considerably better than peak-height calibration curves for this material. The data collection, calculation and display use a shared computer system developed at these laboratories.

1. Introduction

In conventional atomic absorption spectroscopy, a solution containing the elements to be determined is sprayed into a flame. The solvent evaporates and the compounds in solution are decomposed to give an atomic vapour. The measured absorption of light from a hollow cathode lamp emitting the characteristic spectrum of the element sought is then proportional to the concentration of that element in the atomic vapour.

Much more sensitive analysis is possible, however, with the flameless atomizer where a small volume (μl) of solution is placed in an electrically heated carbon cell and the atomic vapour produced by direct heating. A dense population of ground state atoms is produced in the confined absorbance zone, and the residence time within that zone is considerably greater than in the flame, giving detection limits down to 10^{-13} g (10^9 atoms) for the best elements. In practice, the limiting factor in the analysis is often the chemical blank due to reagents, and the instrumental detection limits are not often attainable with the common elements.

Direct analysis of a solid compound eliminates the reagent blank problem and gives greatly enhanced detection limits because of the large increase in effective sample weight. This method has been used by other workers for the analysis of major impurities in such materials as geological samples [1] and metal alloys [2]. This procedure was used by us for the analysis of trace impurities in a number of samples of cadmium mercury telluride (CMT) which is particularly suitable for this approach because of its high volatility. The method was also used to calibrate the response of a spark source mass spectrometer.

The data collection, calculation and display use a real-time shared computer system developed in our laboratories [3].

2. Instrumentation

2.1. Atomic absorption equipment

For this work, the Varian Model 63 Carbon Rod Atomizer was used mounted in a Varian AA5 atomic absorption spectrophotometer with a hydrogen lamp background corrector. This corrects up to an absorbance of about 0.8 for background interference from non-atomic absorption processes, which may be due to molecular absorption or simple light scattering by matrix particles in the cell.

2.2. Computer system

The shared computer system developed and used here is a flexible modular system of hardware and software designed to simplify the interfacing of a remote instrument to a minicomputer (Honeywell DDP 516 or 316) which can be simultaneously used by several remote experiments in real-time mode. Each user is supplied with an interface crate which is connected to the computer by a single co-axial cable used in full duplex at 5 Mb sec^{-1} (Fig. 1).

Interfacing the AA5 to the computer was achieved by using the analogue output of the instrument (0 to 1 V) and an integrating ADC (integration period ~ 2 msec). A simple analogue amplifier is used to adjust the output voltage so that when converted, an absorbance of 1.0 gives a digital reading of 1000. The ADC sampling interval is arranged such that each atomization peak contains about a hundred points and the peak area is calculated by summing these readings. The operator interacts with the computer through a keyboard and storage oscilloscope.

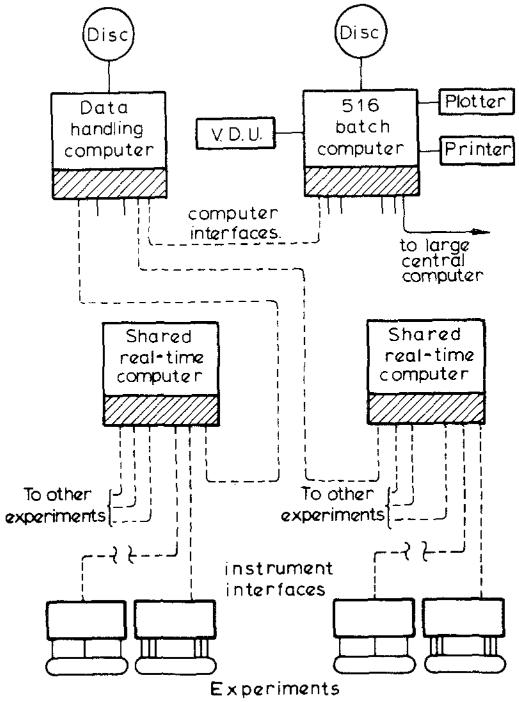


Figure 1 Hierarchical computer system with two real-time computers, a data store, a program-development computer and a link to the laboratory central computing facility. Co-axial cable links.

3. Method

3.1. Setting up

There are three preset stages in atomizing a sample with the Model 63 Carbon Rod Atomizer. The sample is first dried (if added as a solution). Then the temperature is increased until the solid matrix is ashed off. Finally, the temperature is quickly raised to atomize the element being analysed. Time and temperature can be set at each stage to those required for each individual element and optimum conditions established prior to the analysis.

Solution drying conditions were selected on the furnace power supply to give a smooth drying curve. The high volatility of the CMT matrix allows the ash conditions to be adjusted so that all the matrix is removed before the atomizing sequence without volatilizing the element to be sought, although any small residual matrix signal would be compensated for by the background corrector. The final ash temperature of ~ 1100° C was reached by gradually raising the temperature from a lower setting in the first 10 sec to allow the crystal to melt gently.

Atomization conditions varied with the element analysed, but atomization times were between 1 and 3 sec, and temperatures varied from 2000 to 2700° C.

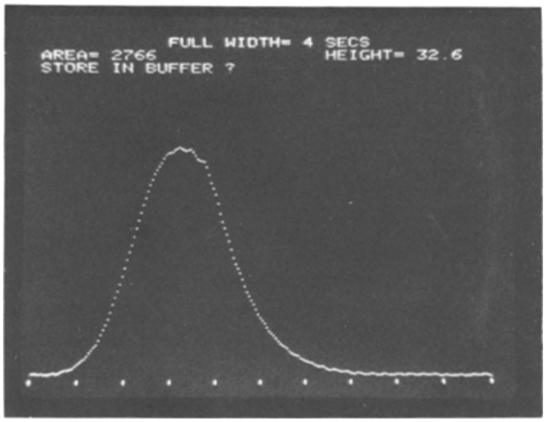
3.2. Analytical procedure

After cutting off the edges of the crystal slice and removing any wax by hot methanol washing, the slice was etched in 5% bromine/methanol for about 2 min to remove surface impurities, and then broken between filter papers to reveal chemically clean surfaces. For the sample determinations up to 10 mg crystal was dropped into the graphite cup in the flameless atomizer and the sample ashed and atomized. Aqueous standards were added to either crystal or ground CMT for calibration purposes.

3.3. Operation and data processing

The computer program is written in DAP and FORTRAN and can be used for either flameless or flame atomic absorption. The whole process is controlled by a question and answer interaction with the operator which ensures that he has appropriate options open to him at every stage.

Two hundred readings are acquired during the atomization period (0.5 to 5 sec). The peak shape, together with peak area and peak height, adjusted to zero baseline, are displayed to the operator (Fig. 2). Peak area values for all standards and samples are stored in the computer and the former



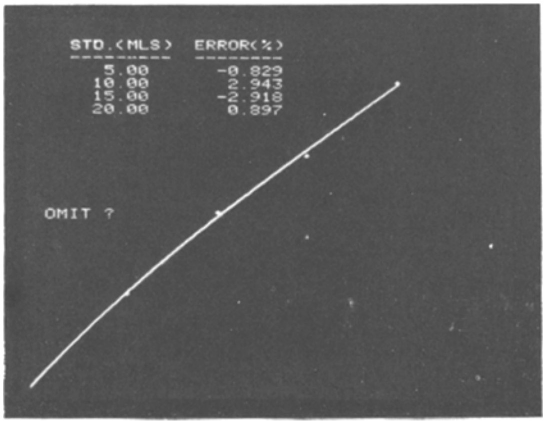
```
                 FULL WIDTH= 4 SECS
AREA= 2766                    HEIGHT= 32.6
STORE IN BUFFER ?
```

Figure 2 Storage monitor display of typical peak.

are fitted to a relative least-squares routine which assumes the curve can be defined by a parametric cubic equation chosen as a result of a comparison of several functions [4]. The fitted curve, together with standard readings and a list of deviations of each reading from the fitted curve, is displayed (Fig. 3). The sample results can be output directly as concentrations in the original solid samples after entering sample weights.

4. Method evaluation

A Cu-doped CMT sample was ground to eliminate possible inhomogeneity, and varying weights were analysed. It was found that area measurements gave a more linear calibration curve than peak height (Fig. 4) implying that peak shape alters with sample weight. Also, the signal given by aqueous Cu standards was not affected by intimate mixing with ground or crystal CMT (Table I) and this was found to be true with all the elements reported.



```
    STD.(MLS)   ERROR(%)
    ---------   --------
       5.00      -0.829
      10.00       2.943
      15.00      -2.918
      20.00       0.897


 OMIT ?
```

Figure 3 Storage monitor display of typical calibration curve.

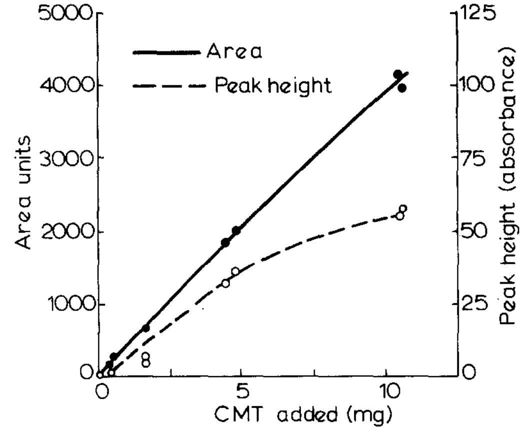


Figure 4 Variation of Cu response with increasing sample weight.

Aqueous standards are very convenient to use and suitable solid standards are rarely available. However, the accuracy of this approach was checked by measuring previously analysed samples of Fe-doped and Ag-doped CMT (the Cu concentration in the samples available was too low to obtain a comparison analysis by another technique).

A value of 19.5 ppmw Fe had been found in the Fe-doped CMT by flame atomic absorption. Because the concentration was high for the solid sample determination, a less sensitive Fe absorption line was used (372.0 nm, which is at least 10 times less sensitive than the primary absorption line) and low sample weights had to be taken. The sample was finely ground and varying weights added to the sample cup, comparing them with a range of aqueous standards (Fig. 5). The analysed Fe value was used to give the concentration axis for the solid sample curve.

As can be seen, the aqueous standards gave a very nearly linear fit up to a peak area of about 5000 (absorbance about 0.7). The solid CMT calibration shows more curvature but the two curves are very similar considering the big difference in sample type. The mean percentage deviation of all the solid sample values from the solid standard curve (which gives a measure of the precision) is 8.3% while the deviation of the solid sample values from the aqueous standard curve is 13.5%.

It should be remembered that because we were only able to use low sample weights, i.e. 0.2 to 1.5

TABLE I Area under peak (corrected for blanks)

970 ng Cu	3911
970 ng Cu + 10 mg ground CMT	3730
970 ng Cu + 10 mg crystal CMT	3806

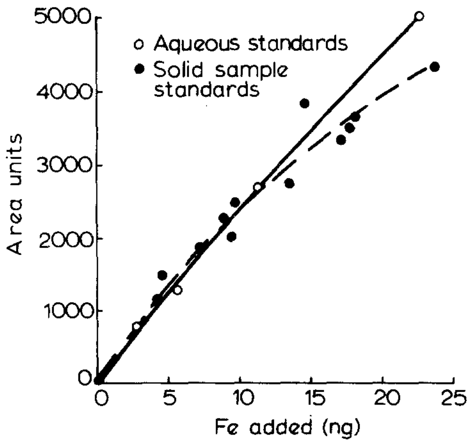


Figure 5 Comparison of aqueous standard and solid standard calibration data (Fe).

mg, with these high impurity levels, the transfer of solid samples becomes a problem (powders would be expected to be worse than crystals). The precision could very easily be better than this for lower dopant levels where more sample could be taken. Although for the best precision, a solid sample of known concentration is best for calibration purposes, in practice at the concentration levels obtained in this material this is rarely possible, However, this experiment shows that aqueous standards give nearly as good a figure for Fe determination.

Ag was measured in another doped sample by the carbon rod solution technique and gave a value of 0.2 ppm. The same sample measured by the solid sampling technique, using aqueous standards, gave a value of 0.23 ppm.

Limits of detection attainable are excellent and are given in Table II, assuming a 10 mg sample weight.

TABLE II

Element	Detection limit (ppmw)
Ag	0.000 2
Cu	0.002
Fe	0.001
Mn	0.000 2
Cr	0.002
Al*	0.004
Na	0.000 1
Mg	0.000 06
Si*	0.01

* Detection limits obtained with tube furnace.

4. Conclusions

The solid sampling technique for flameless atomization has been found to be easily applied and extremely sensitive. It is probably 1 to 2 orders more sensitive than the flameless solution method with less sample per element required and no reagent blank problem. Accuracy and precision of the results was good. It is known that calibration curves of integrated peak areas are generally linear over wider ranges of concentration than peak height measurements for solution standards [5]. We have shown area measurements to be considerably better than peak-height calibration curves for solid CMT samples.

Aqueous standards have been used throughout. This is justified by comparing the solid sampling technique with results obtained by solution techniques where the standards are carefully matched to sample matrix and acid content, e.g. Fe and Ag. Also the addition of CMT to aqueous standards of all the other elements did not alter the absorbances obtained.

The on-line computer system allows greater ease of operation and direct integration of peaks produced by the transient signal generated by the operation of the carbon rod atomizer, as well as peak-height measurement. In particular, the visual display of the "atomize" period makes identification and separation of the atomic peak from possible interfering peaks (e.g. emission) very much easier and more reliable.

The easiest and cleanest method of sample addition is by adding discrete pieces of crystal and this is useful for monitoring changes in dopant concentration in a crystal slice since small samples of crystal can be analysed individually. There is minimum chemical preparation needed and using larger pieces of crystal will reduce the contribution from surface impurities. Spark source mass spectrography gives a broad coverage of the elements in CMT but it cannot attain the precision of this technique, and some element lines are masked by interferences. This technique is one of the few practical methods for quantitative analysis in the ppb region and was used to calibrate the response of the MS7 mass spectrograph.

Acknowledgement

We would like to thank Mr B. Bartlett and colleagues at Mullard Southampton for supplying the materials used in this work.

References

1. F. J. LANGMYHR, *Talanta* **24** (1977) 277.
2. J. Y. MARKS, G. G. WELCHER and R. J. SPELLMAN, *Appl. Spectrosc.* **31** (1977) 9.
3. M. R. BOUDRY, J. A. MORICE and E. J. MILLETT, *Biomed. Comp. Tech.* April (1976) 48.
4. J. A. MORICE, private communications.
5. R. E. STURGEON, C. L. CHAKRABARTI, I. S. MAINES and P. C. BERTELS, *Anal. Chem.* **47** (1975) 1240.

Received 23 October and accepted 20 November 1978.