Acquisition and analysis of GFAAS data

M. J. Adams,* G. J. Ewen and C. A. Shand
The Macaulay Land Use Research Institute, Craigiebuckler, Aberdeen AB9 2QJ, UK

Since its inception as an analytical technique some 30 years ago atomic absorption spectrometry has become a firmly established method for the analysis of trace metals. Graphite furnace atomic absorption spectrometry provides the analyst with the capability of analysis of solutions containing µg l⁻¹ levels of the analyte, but, because of the transient nature of the signals, a sophisticated approach to the data acquisition and handling of data is required. Most modern commercial graphite furnace atomic absorption spectrometers have built-in microprocessors for this purpose but they often have limited capability for extensible user programs and limited data storage facilities. In this communication we describe the use of an Apple IIe microcomputer for the acquisition of data from a Pye Unicam SP9 graphite furnace atomic absorption spectrometer. Details of the interface which utilizes an in-house designed AD converter, and an overview of the Pascal and assembler programs employed are given. The system allows the user to record, store and dump the graphical display of the furnace signals for all analyses performed. Files containing details of peak height, and area are formatted on an eight-column spreadsheet. Details of sample type, concentrations of standards, dilutions and replication are entered from the keyboard. The calibration graph is constructed using a moving quadratic fit routine and the concentrations of the analyte in unknown solutions calculated. In addition to this, greater processing power and integration of the data into other analytical schemes can be achieved by exporting the data to other software packages and computers. Details of data transfer between the Apple IIe and an Amstrad PC 1512 are given. Some examples of the use of the system in the development of an analytical method for silver in plant material are given.

Introduction

Atomic absorption spectrometry (AAS) is an established analytical technique, which is routinely employed in many analytical laboratories for the determination of trace quantities of metals in solutions [1]. Since its development by Walsh over 30 years ago the growth in the application of AAS has become part of the trend towards increasing use of instrumentation in chemical analysis. The first commercial AAS instruments were introduced in the early 1960s and generally employed flames as cells for the production of analyte atoms. The flame is still the most common atom cell for routine analyses and, in general, analytical sensitivities range from µg l⁻¹ to mg l⁻¹. If greater sensitivity is required, or the sample size is inadequate for nebulization into a conventional flame system, then non-flame techniques can be employed. Of these, the most widely used is graphite furnace atomic absorption spectrometry (GFAAS). An increase in sensitivity of between one and three orders of magnitude can be realized for most elements using GFAAS compared with flame AAS procedures. GFAAS has some disadvantages compared with flame AAS. The duration of the analytical signal from a flame system can be extended to any convenient period, provided there is sufficient sample, and the signal can be integrated over this time to achieve a high measurement precision. The signal produced by electrothermal excitation in GFAAS, however, is transitory and requires a more sophisticated approach to the techniques of data capture and recording. Continued improvements and refinements of instrumentation, in particular the application of microelectronic technology, have removed or reduced many of the problems associated with early GFAAS techniques. Most modern commercial instruments used for GFAAS have some built-in microprocessor-controlled unit for recording the analytical signal and many have sophisticated graphic display output facilities and video screen to show the signal trace, the shape of which can be a useful aid in optimizing and monitoring the analytical procedure.

The built-in microprocessors associated with most commercial analytical instruments are programmed to attend to routine tasks and have only limited capability for extensible user programs and, usually, they provide minimal data storage facilities. Where greater data processing facilities are required and there is a need to store data and provide an integrated data management scheme within a laboratory environment, then interfacing the instrument to a personal microcomputer can present the user with a more flexible and extensible analytical system. A wide variety of inexpensive personal computers are available and most are capable of being interfaced to analytical instrumentation. One such machine, which has found extensive application in many laboratories, is the 8-bit Apple II microcomputer.

In this communication we describe the use of an Apple IIe microcomputer for the acquisition and recording of analytical data directly from a Pye Unicam SP9 Video Furnace AAS system (Pye Unicam Ltd, Cambridge, UK). The details of the computer-spectrometer interface are provided and the use of the system is illustrated with typical results obtained from an optimization study of the determination of silver in plant material. An overview of the Pascal and assembler programs employed in the data logging and manipulation procedures is provided. The transfer of data acquired by the Apple IIe from the spectrometer to a second microcomputer operating a commercial spreadsheet and graphics programs is also described.

---

Present address: Dr M. J. Adams, School of Applied Sciences, The Polytechnic, Wulfruna Street, Wolverhampton WV1 1SB, UK.

© 1988 The Macaulay Land Use Research Institute.
Instrumentation

The commercial atomic absorption spectrometer employed is a Pye Unicam SP9 system complete with a PU9095 video furnace programmer, a PU9090 data graphics system and SP9 furnace autosampler. The SP9 is a single-beam spectrometer in which background correction for non-specific absorption is achieved with the aid of a deuterium-filled hollow cathode continuum source which is pulsed alternately with the analyte's hollow cathode lamp. The intensity of the analytical signal output from the photomultiplier is converted to absorbance using a logarithmic amplifier and this signal is output to the data graphics system. In conjunction with the video furnace programmer this data processing system can display 'cookbook' details of analytical conditions for the elements determinable by AAS. In addition, the graphics facilities of the video programmer permit the display of the transient peaks observed in GFAAS studies and the calibration plots for the analytical standards employed. Autosamplers are a desirable addition to any GFAAS system both to improve measurement precision and enable automation of the analytical procedure to be achieved. The SP9 furnace autosampler employed here accepts up to 38 sample cups and two wash cups.

The microcomputer employed to interface to the SP9 system was an Apple IIe. This microcomputer has proved to be a popular choice for laboratory applications largely because of the ease with which interface and expansion circuits can be accommodated within the microcomputer. The Apple IIe machine uses a 8-bit microprocessor (Type 6502) as the central processing unit and can directly access up to 64K of memory, which can be expanded to 128K using page-switching techniques. As standard, the computer was equipped with dual floppy disk drive units, a video monitor and an Epson FX-80 printer. Interface circuit cards were installed in the computer using its backbone bus structure; several edge connector slots are available for these boards. All the computer software was written under the Pascal UCSD Operating System.

Interfacing

The general interfacing scheme is illustrated in figure 1. The spectrometer was connected to the microcomputer via an analogue-to-digital (AD) converter within the computer and its so-called games socket which served as a TTL trigger detector. The AD converter was designed and constructed in-house and has been described in detail elsewhere [2 and 3]. It comprises a precision 12-bit CMOS AD574 integrated circuit (Analog Devices) which can complete a 12-bit data conversion in about 25 μs. This device and all other components, including the X10 signal amplifier, were mounted on a single circuit board for direct connection to the computer using one of its input/output expansion slots. The AD converter was operated in a unipolar mode, 0–10V FSD. The analogue analytical signal was taken directly from the spectrometer. Normally, this signal is supplied as a voltage in the range 0–10 mV, corresponding to 0–1 Absorbance Units, for use with a standard analogue chart recorder. To eliminate potential problems due to electrical pick-up on the spectrometer-computer cable the absorbance and scale expansion circuit board within the spectrometer was modified to provide a 0–1V analogue output. This was achieved by bypassing an internal signal attenuator circuit.

In employing analogue signals for digital data acquisition programs, special care must be taken to control the initiation of the data logging procedure and the rate at which data is accumulated. In the application discussed here the cycle start pulse was obtained from the recorder socket of the video furnace programmer. This signal is conventionally used to activate a high-speed chart recorder, which can be employed to monitor the transient
analytical trace. This signal (0/5V TTL) was led to the
games socket of the Apple computer. The rate of data
acquisition was under program control and selected to
achieve about 450 readings in the maximum 9s analytical
measurement period.

The microcomputer interfacing and data acquisition
software was written in Pascal with the AD conversion
routine being prepared as assembly code and called from
the main program as an external function. Once initiated,
this program strobes the computer keyboard and the
TTL (games) socket to test if a quit key has been pressed
by the operator or if an analytical program has been
started from the video programmer. If an analytical cycle
is initiated then digitization and recording begins. The
spectrometer system is programmed to provide a 7s
delay for zeroing period prior to firing the graphite furnace
and during this period 350 digital readings are recorded
and averaged by the Apple computer to provide a mean
background reading which is subtracted from each point
of the resultant analytical AAS trace. The AAS data is
recorded until the trigger signal is deactivated as
programmed at the video furnace programmer. Following
each analytical cycle the Apple computer scales the
AAS data and presents the complete trace on its graphics
display unit along with the maximum signal recorded
(peak absorbance) and the signal area (absorbances). The
trace data is stored in a disk file after each analysis to
minimize data loss should there be a program crash or
any loss of electrical power to the computing system. The
whole procedure is repeated until the quit key is pressed
by the user. When the data acquisition program is exited the
analytical data in the disk file is re-formatted to
provide a data file containing the peak height and area
data and a graphics file containing the original data for
the profile of the trace. These files can be used for
subsequent calibration and manipulation programs
within the Apple computer or exported to other computer
systems. A second computer, an Amstrad PC1512, was
employed for off-line processing and management of the
analytical data. The Apple microcomputer was connec-
ted to the PC via a serial, RS232C, interface link. Data
transferred to the PC could be studied using a wide range
of commercial software packages and integrated with
other analytical and management data in this second
microcomputer.

Data processing and analysis

The principal data processing software for manipulating
and analysing the pre-recorded GFAAS data is an
in-house program, DataCalc. DataCalc loads the analyti-
cal data into computer memory and displays it on screen
page at a time, on the video monitor. The format of the
display is similar to many of the common spreadsheet
programs, viz. the analytical data occupies discrete rows
and columns in the screen. The user can move a cursor
from cell to cell between columns in a record and between
records or rows. The data can be edited, listed on the
printer and saved back on floppy disk for storage and
future processing operations. Data processing commands
include the determination of the analytical calibration
curve and fitting the sample absorbance data to this
curve. The command structure of DataCalc is illustrated in
figure 2.

As well as the date and filename, displayed on the top row
of the screen, up to 16 records (rows) of analytical data,
formatted in eight columns, are displayed at any time.
These data columns provide the record (sample) number,
class, replicate code, dilution factor, analytical signal
peak height and area and the computed, or user-entered,
concentrations. The record class defines the nature of the
sample as being a standard, unknown, blank or null. Any
record marked by the user as being null is ignored by the
computer in subsequent calculations. Analyses by
GFAAS are rarely performed singly. Sample duplication
is usually encountered and to indicate this replication, the
program permits an integer replicate code to be used to
indicate similar solutions, the absorbance or concentra-
tion values of which will be automatically averaged. The
peak height and area fields contain integer values
corresponding to the analytical instrument’s signal out-
put, as digitized by the computer (these values can be
entered by the user if the program is used in isolation from
the spectrometer). The concentration column contains
either values for standards keyed-in by the user or values
computed following calibration.

The major function of the DataCalc processing package is
to compute an analytical calibration curve from the
standards’ data and calculate previously unknown sam-
ple concentrations by interpolating their measured signal
absorbance values on the standard curve. The set of
standards’ records is sorted into an order of increasing
concentration, using a simple bubble-sort routine, and
the curve-fitting coefficients are calculated. The proce-
dure adopted to compute the calibration graph is similar
to that employed by the spectrometer manufacturers and
detailed by Whiteside et al. [4]. The average absorbance
value determined from all designated blank solutions is
subtracted from all other absorbance data and a straight
line is fitted between zero and the first standard. A
quadratic function is then fitted between every subse-
quent pair of data points, a third fitting point being
calculated using extrapolated slopes. This ‘moving-quad-

Figure 2. The command structure of the Pascal DataCalc
spreadsheet program used to analyse the GFAAS data.
Figure 3. Screen dump of calibration curve for silver.

A Pascal program can be selected to transmit the analytical data from the Apple machine to the PC system. The user is prompted to select the transfer of absorbance profile graphics, data or the analytical spreadsheet data. Communication is achieved between the two microcomputers using ‘Kermit’, a de facto standard protocol for inter-computer information transfer, operating on the PC. Controlled by the PC the data is output from the Apple and recorded as a text file on a PC disk. This data is available for subsequent analysis.

Applications

The main function of the computerized system is to collect raw data from the atomic absorption instrument, compute the analytical calibration curve from the standards and calculate the concentration of the analyte in unknown samples. In addition to this routine operation, however, the facilities offered by the microcomputer are valuable during the development of new furnace analytical programs. An example of the use of the system in the development and application of a method for the analysis of silver in nitric acid extracts of ashed sphagnum moss is described.

The first stage in the development of GFAAS methods often involves a series of measurements with standard solutions of the analyte to determine the optimum conditions for the pyrolysis and atomisation steps of the furnace program. Figure 4 shows the profiles for the atomization of 0.1 ng Ag (applied as AgNO₃ in 2% HNO₃) at 1800 °C from a totally pyrolytic graphite tube and platform combination following pyrolysis at different temperatures.

A comparison of the profile obtained at a pyrolysis temperature of 340 °C with that at 490 °C shows the appearance of an additional early peak. This is indicative of a slight loss of silver from the platform to the tube wall during pyrolysis. This deduction was confirmed by the atomization of Ag from the wall alone, see figure 4(d). As the pyrolysis temperature is increased further, to 685 °C, there is in addition to loss from the wall to the platform, a substantial loss of analyte from the atom cell resulting in a decrease in peak height and area. The pyrolysis temperature selected for further work on Ag, applied as nitrate, was 340 °C.

The use of a host computer running a commercial spreadsheet program ‘Symphony’ is illustrated in figure 5. This shows an overlay of the absorbance profiles for the atomization of 0.1 ng Ag at different temperatures. In this case the data has been re-scaled (DataCalc scales all points to fill the page) using the spreadsheet commands of Symphony. The effect of increasing the atomization temperature on the relative positions and shapes of the signals is clearly illustrated. As the atomization temperature is increased peak height increases sharply and no plateau is reached in the range studied. Peak area measurements exhibit a slight decrease as the temperature is increased, probably due to increased diffusion losses. For subsequent analyses a compromise atomization temperature of 1800 °C held for a period of 5s was
Figure 4. Absorbance profiles for atomization of 0.1 ng Ag at 1800°C. (a) following pyrolysis at 340; (b) 490; and (c) 680°C using a totally pyrolytic tube and platform; and (d) following pyrolysis at 340°C using a tube alone.

used. This example of the use of a powerful spreadsheet program such as Symphony serves to illustrate the principle of data transfer and use within a laboratory and has many potential applications. Where a detailed study or mathematical treatment of absorbance profiles is to be conducted, for example kinetic modelling of the atomization process, a variety of commercial programs are available. Similarly, the range of data-base packages commercially available for microcomputers makes the in-house development of such programs largely unnecessary. They can form the basis of sophisticated laboratory data management systems which can readily link to the dedicated microcomputer application as detailed here.

Conclusion

A microcomputer system has been described which interfaces to a commercial electrothermal atomic absorption spectrometer for the direct acquisition and subsequent manipulation of the analytical data. As described above, an important advantage of this computerized system is that a full record can be maintained of the absorbance versus time profiles for all the solutions analysed. This information is invaluable in designing new analytical procedures when it is necessary to monitor the effects on the analytical signal of, for example, different ashing and atomizing temperatures. The computerized storage of the graphic trace information also permits the user to check an analysis where a fault is suspected to have occurred in the graphite tube system.

The absorbance peak height and area data are recorded in the computer system for calibration and analysis using spreadsheet-type software. In many cases no further manipulation of this data is required other than that supplied by the in-house designed programs. Where the AAS analysis, however, forms a part of a wider analytical scheme involving other techniques and other laboratories, the GFAAS data recorded by the microcomputer system can be transferred via a simple asynchronous serial interface to other computer systems. An example of GFAAS data manipulation using a commercial spreadsheet package on a PC computer has been presented.

References

1. Van Loon, J. C., Selected Methods of Trace Metal Analysis (John Wiley and Sons, New York, 1985).
2. Ewen, G. J. and Adams, M. J., Laboratory Practice, 33 (1984), 116.
3. Adams, M. J. and Ewen, G. J., Journal of Automatic Chemistry, 6 (1984), 202.
4. Whiteside, P. J., Stockdale, T. J. and Price, W. J., Spectrochimica Acta, 35B (1980), 795.