



Figure 1. Diluter with piston at upper stop

required number of dilutions is obtained. The apparatus is taken apart for cleaning by removing the bar which holds the adjustable upper stop.

Calibration of the apparatus can be accomplished by successive fine adjustments, once a dilution factor is chosen and approxi-

mately set by fixing the upper and lower stops. The volume of the stir bar must be subtracted from the residual concentrated standard volume in fixing the bottom stop, and the unmixed solution in the needle must be considered in setting the volume of diluent added by fixing the top stop. These approximate settings can be made using the calibration marks on the syringe or by weighing the apparatus empty and filled to the top and bottom stop. Fine adjustments are made by turning the upper stop screw and measuring the resultant change. Dyes or salt solutions can be used to determine the dilution factor optically or gravimetrically.

RESULTS AND DISCUSSION

Table I gives the results of a series of dilutions determined gravimetrically using a solution of sodium chloride as the standard. The solutions, including the most concentrated, were received directly into pre-weighed pans, dried in an oven and weighed again. The dilution apparatus had been previously adjusted using a dye and fluorometer to fix it at a dilution of 1 to 1. Ten repetitive weighings of pure water indicated that 7.51 mL were delivered for each dilution; the volumetric error was less than 0.1%. The diluent reservoir was placed on top of a cabinet giving about a 2-m water head which was sufficient to force the piston to rise to its upper stop when the three-way valve was turned to admit diluent. Since this apparatus does not require the complete rinseout of the solution being diluted, as is the case in most sampler dilutors, it is possible to make dilutions with small additions of diluent to a larger volume of concentrated standard. Since the syringe and stops are not particularly expensive, a given dilution factor may be permanently fixed by cementing the adjustment screw in place.

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Preparation and Characterization of Glass Beads for Use in Thermionic Gas Chromatographic Detectors

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Alkali thermionic detectors have been used for many years in gas chromatography but they have been notoriously difficult to work with because careful control of all detector parameters is necessary to obtain reproducibility. The use of ceramic elements for halogen detection has been previously described (1). Recently, a new version of this detector has appeared (2, 3) which utilizes a small glass bead containing rubidium (oxide or silicate). This bead is positioned within 0.5–1.5 mm of the flame tip and is maintained at a negative potential. The detector can be operated in a nitrogen-phosphorus (N-P) mode or in a phosphorus (P) mode by changing the flow rates of hydrogen and air as well as the potential applied to the flame tip. The bead is heated electrically and, thus, careful control of the volatility of alkali atoms in the glass can be achieved. Our recent studies of the response of this detector have shown that, if the bead current is carefully controlled, the detector is very reproducible (4).

During our studies aimed at characterizing the detector, these beads were found to have lifetimes of only about 3–4

months, so numerous beads were utilized. As a result, an effort was made to produce these beads in the laboratory. Unfortunately, a description of the glass composition and the procedure of the beads was not available. Hence, we examined the behavior of several different compositions. Furthermore, we wanted to see if the sensitivities and specificities could be modified by changing bead composition.

This paper describes a simple procedure for preparing the beads using materials having a cost of about \$1.00 per bead. The most important characteristics of the beads are also given.

EXPERIMENTAL

Chemicals. Amorphous silica (Illinois, Mineral Co., Cairo, Ill.), grade 200, was used in preparing beads 5–8. Beads 1–3 were prepared from finely ground Corning glass 7740 (Pyrex). Sodium carbonate (Baker Analyzed reagent) was added as a flux to beads 1 and 6–8. Boric acid (Baker Analyzed reagent) was also used as a flux in beads 6–8. Sodium borate decahydrate (Baker Analyzed reagent) was used in making bead 5 and thus the sodium-to-boron ratio was fixed. Rubidium nitrate (Fairmount Chemical Co., Newark, N.J.) was used in beads 1–3 and 5–7. In the case of bead 8, cesium fluoride (Peninsular Chemical Research, Gainesville, Fla.) was used instead of rubidium nitrate. All beads were fused to a platinum wire (Fisher Scientific, Atlanta, Ga.) having a diameter of 0.020 cm whereas the commercial bead was mounted on 0.025-mm wire.

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Table I. Characteristics of Glass Beads

Property	Oper- ating Mode	Bead No.							
		1	2	3	4	5	6	7	8
Composition									
%SiO ₂		61.1	69.1	69.1	- ^d	60.0	94.1	68.2	69.5
%B ₂ O ₃		9.79	11.1	11.1	-	24.5	1.14	2.80	1.95
%Na ₂ O		14.4	3.30	3.30	-	10.9	-	7.90	8.65
%K ₂ O		0.30	0.33	0.33	-	-	-	-	-
%Al ₂ O ₃		1.70	1.90	1.90	-	-	-	-	-
%Rb ₂ O		12.7	14.4	14.4	-	4.53	4.73	21.1	-
%Cs ₂ O		-	-	-	-	-	-	-	20.0
Current range									
Heating, A	N-P	3.98-4.13	3.90-4.30	4.10-4.40	2.70-3.50	2.80-3.50	3.99-4.30	3.90-4.11	3.40-3.90
Bead, pA	N-P	0.40-9.0	0.50-7.00	0.50-7.00	0.50-10.0	0.50-7.00	0.10-1.00	0.20-10.0	2.5 -10.0
Sensitivity									
Azobenzene, C/g × 10 ⁻²	N-P	2.41	1.91	2.30	1.06	5.40	0.184	4.50	2.85
Malathion, C/g × 10 ⁻¹	N-P	4.91	1.89	1.96	0.960	-	0.330	6.55	2.45
Ratio ^a	N-P	20.4	9.92	8.52	9.06	-	17.9	14.6	8.60
Ratio ^b	N-P	24.5	15.9	13.4	9.06	-	26.6	15.6	17.7
<i>n</i> -Hexane, C/g × 10 ⁻⁸	N-P	2.1	1.3	-	2.8	1.3	0.66	4.3	3.8
Azobenzene, C/g × 10 ⁻³	P	3.35	0.933	0.179	3.10	-	0.0672	42.5	-
Malathion, C/g × 10 ⁻¹	P	1.14	1.48	0.132	2.01	-	0.120	6.91	0.102
Ratio ^c	P	34.0	159	73.7	64.8	-	179	16.3	-
<i>n</i> -Hexane, C/g × 10 ⁻⁶	P	9.3	-	-	21	-	-	12	19
Detectability, g/s × 10 ⁻¹³									
Azobenzene	N-P	75	86	52	110	-	330	22	49
Malathion	N-P	3.7	8.7	6.1	12	-	18	1.5	5.7
Azobenzene	P	180	880	-	130	-	8900	19	-
Malathion	P	5.3	5.5	-	2.0	-	50	1.1	118
Linearity, × 10 ³	N-P	4.1	-	-	3.0	-	-	11.0	3.2
Loss of bead current, %/h	N-P	6.2	5.3	5.8	5.1	~12	3.0	4.0	5.2

^a Sensitivity ratio: malathion/azobenzene at 7.8 pA. ^b Sensitivity ratio: malathion to azobenzene at 3.0 pA.

^c Sensitivity ratio: malathion to azobenzene. ^d A dash indicates that a particular measurement was not made.

Malathion and azobenzene were used as model compounds for characterization of the beads. Malathion, *S*(1,2-dicarboxyethyl)-*O,O*-dimethyldithiophosphate (American Cyanamid Co., Princeton, N.J.) having a purity of 99.3% was dissolved in *n*-hexane (Nanograde, Mallinckrodt, St. Louis, Mo.). The concentration of the solution was 5 ng/μL. Solutions of azobenzene (Eastman, Rochester, N.Y.) in *n*-hexane were prepared containing 0.05, 0.5, 5, 50, 500 and 5000 ng/μL.

A glass column, 183 cm × 2 mm i.d., containing 3% OV-1 on 90-100 mesh Gas-Chrom Q (Applied Science Labs., State College, Pa.) was used. Nitrogen (Selox) was purified by passage through molecular sieve and silica gel. Air and hydrogen (Selox), purified by passage through molecular sieve and silica gel, were used as auxiliary gases for the flame ionization detector and the nitrogen-phosphorus detector.

Apparatus. A Perkin-Elmer nitrogen-phosphorus detector was used on their Model 3920 gas chromatograph. All of our beads were mounted in the Perkin-Elmer bead assembly. The heating current was measured by placing a 0-10A ammeter (Weston, Newark, N.J.) in series with the bead. A flame ionization detector mounted in parallel with the nitrogen-phosphorus detector received 48.5% of the injected sample. The output of the electrometer was fed to a Linear Instruments Co. dual-pen recorder (Irvine, Calif.).

Procedures. Bead Construction. The glass mixture was prepared by weighing the silica, the fluxes, and either the rubidium nitrate or cesium fluoride. The weight of the total mixture was kept at about 2 g. The percentage composition of each bead prepared is given in Table I. Beads 1-3 were made by using ground Corning glass 7740 and subsequently adding sodium carbonate (bead 1) and rubidium nitrate (beads 1-3). Again, the total weight was kept at about 2 g. To calculate the final composition of the latter beads, the original composition of Corning 7740, as reported in the literature, was used (5). The weights of all components in the mixture are reported in Table I as the oxide, a common practice in reporting glass composition (5).

The weighed mixture was transferred to a 15-mL Coors porcelain crucible. Using a natural gas-oxygen rich mixture and a blow pipe torch (National 3A, Atlanta, Ga.), the powder mixture

was melted and stirred with a quartz rod. At this point, a thin strand of glass was pulled from the melt. The strand was later used to make the bead. The fused glass mixture could be left in the crucible and reheated at a later time to obtain additional strands. The mixture for making bead 6 was melted using an oxyacetylene "Rose-bud" heating tip (Meco-Wg-1) because its low sodium content resulted in a very high melting material.

A 1.5-cm section of the 0.020-mm diameter platinum wire was shaped in the form of an arch and secured in a vise. A 7 cm × 0.159 cm piece of stainless steel tubing was inserted into the tip of the torch. The torch was lit and the natural gas-oxygen mixture was adjusted so that the flame was no longer than 0.5 cm. The tip of the strand of glass was brought to the flame and held there long enough to form a bead no larger than 1.5 mm in diameter. The platinum and bead were heated again and brought together to attach the bead to the wire. By reheating the bead and the strand of glass, they could be reunited to adjust the size of the bead. The bead was then reheated and the heat maintained long enough for the wire to reach the center of the bead. The bead always assumed a nearly spherical shape with a slightly shorter transverse axis. All beads had dimensions of 1.4 × 1.6 mm and weighed about 4 mg. However, bead 3 was made by adding additional glass to bead 2 until the bead was 1.8 × 2.0 mm. A magnifying glass provided with a mm scale was used to measure bead size. The entire step of attachment and centering of the bead on the wire required only about 5 min.

The wire-bead assembly was then spot-welded to the Perkin-Elmer bead assembly holder. After installation, the beads were conditioned by passing sufficient current to cause the bead to glow with a medium red color. The conditioning period for beads 1-7 lasted from 1-24 h. During the conditioning period, the bead current (background current) reached values of about 200 pA. The sensitivity toward either malathion or azobenzene was quite low and the detector was almost useless. However, after the bead had been conditioned, the bead current usually reached about 1 pA and gave sensitivities typified by those in Table I. One exception to that behavior was bead 8 for which details will be discussed later.

Bead Current. All beads were tested in the range of 0.50-10.0 pA because we have previously shown (4) that a 10-pA bead

current was the best compromise between sensitivity and bead lifetime. All beads, except bead 6, were capable of delivering currents greater than 100 pA. Bead 6, which had a high silica concentration, low boron and low rubidium concentration, showed a short range of bead current.

Heating Current. The heating current was dependent, among other variables, upon the cross-sectional area of the wire. The wire used in this study was slightly smaller than that used in the commercially available bead. Thus, the heating currents were higher due to the increased heat-loss. The heating current was also a function of the bead composition since, in the molten state, the bead conducted electricity. Thus, it was observed that a high boron content and the presence of cesium led to low bead currents at lower heating currents. The importance of achieving a low heating current lies in the fact that the power supply was current-limited so it would shut off at currents of about 4.6 A.

Gas Chromatography. Each bead was characterized in the N-P mode and in the P mode. In the N-P mode, hydrogen flow was kept constant at 2.60 mL/min while air was maintained at 83.5 mL/min. In the P-mode, hydrogen flow was 23.1 mL/min and air was kept at 240 mL/min. The heating current in the N-P mode was adjusted as shown in Table I so as to obtain a bead current in the range of 0.1–10 pA. However, since the beads did differ substantially in the P mode, a heating current was selected so as to obtain a sensitivity of about 0.1 C/g. A more detailed description of these two modes of operation has been recently prepared (6).

The detectors were maintained at 260 °C, the column at 190 °C, and the injector at 260 °C. The carrier gas flow rate was 80 mL/min. The samples were injected using a Hamilton 75N-5 μ L syringe (Supelco Inc., Bellefonte, Pa.). The injection volume was kept constant at 3.2 μ L. The areas were obtained from the mean of two injections except when measuring the reproducibility of response when larger numbers of replicates were used.

Calculations. None of the column or operating parameters were changed during the study. The peak shapes for azobenzene and malathion were very symmetrical. Thus, the peak areas were obtained by the product of height and width at half height. The peak areas were expressed in terms of coulombs (C) and divided by the mass injected. Thus, the sensitivity as defined by Hartmann (7) was used as one of the criteria for characterization. Ratios of sensitivities at bead currents of 3.0 and 7.8 pA were also calculated. This ratio indicated the specificity of the detector (7).

Noise measurements were made with the recorder and expressed in amperes. The detectabilities were calculated as twice the noise divided by the sensitivity (7).

Linearity ranges were determined by a semilogarithmic plot of sensitivity vs. logarithm of the mass injected. The slope of this plot should be zero. The upper limit was the mass that yielded a response which deviated from linearity by an arbitrarily defined 5%; the lower limit was the mass where the signal was equal to twice the size of the noise. The linearity range was the ratio of the upper limit to the lower limit.

Stability of the detector with different beads was calculated by measuring the bead current for 12–14 h. The loss in bead current per hour was expressed as a percentage of the original bead current. All beads were subjected to a reproducibility test by injecting azobenzene and malathion over a 5–6 h period. During that time, the bead current was maintained constant by increasing the electrical heating.

RESULTS

In the early part of our preliminary studies, we fashioned several batches of Borax beads after those used in classical "bead tests". We soon found that the size of the bead influenced both the sensitivity and the selectivity, as will be documented later. However, when the size of the bead was carefully controlled, as described in the Experimental section of this paper, the characteristics for beads made from three replicate batches were found to disagree a maximum of 10%, even though the bead composition was that which was later found to have the least stable response (No. 5, Table I). Hence, we felt confident that when beads of the same size were compared under the same operating conditions (4, 6), large

differences in their operating characteristics could be assigned, with a high degree of confidence, to differences in the compositions of the beads.

Sensitivity Studies in the N-P Mode. The plots of sensitivity vs. bead current for the commercial beads were linear for azobenzene in the range of 1–150 pA and for malathion in the range of 1–50 pA (4, 6). However, the beads made in our laboratory showed linear plots of sensitivity vs. bead current for azobenzene only in the range of 1–10 pA, and for malathion, in the region of 1–4 pA. Thus, when the sensitivities are compared in Table I at bead currents of 3.0 and 7.8 pA, one expects to find a higher sensitivity ratio of malathion to azobenzene at 3.0 pA than at 7.8 pA. This characteristic is not necessarily a disadvantage because it permits one to control to a certain extent the specificity by means of the bead current. At present, we do not have an explanation for this difference except that it is related to the composition of the beads.

Bead 7 which contained the highest rubidium content, showed the closest behavior to the commercially available bead. This is reflected by the fact that ratio of sensitivities at the two currents differed by less than 7%.

Bead 5, which had the highest percentages of boron oxide and sodium oxide, showed the greatest sensitivity for azobenzene. However, this bead was not extensively studied since it suffered drastically from losses in bead current over short periods of time. Sensitivity toward azobenzene did not show a trend with increasing boron oxide concentration alone. However, it is significant that the three most sensitive beads 1, 8, and 7 all had a ratio of Na_2O to B_2O_3 greater than unity. Hence, sodium in conjunction with boron appears to lead to high nitrogen sensitivity. Bead 7, which had a high concentration of rubidium, also had a high sensitivity toward azobenzene. Replacing rubidium by cesium also yielded a nitrogen sensitivity. However, the azobenzene sensitivity did not necessarily increase with rubidium concentration as can be seen from beads 1 and 2.

Bead 6, which had a high silica content but no sodium, showed the lowest sensitivity for azobenzene. That result is not surprising considering that this bead was capable of generating only very low bead currents. This bead also had one of the lowest rubidium contents.

The sensitivities of the beads toward malathion followed the same order as that for azobenzene. An exception was the reversal in which bead 1, a Pyrex glass with added sodium, showed higher sensitivity than bead 8, which contained a high cesium content. The opposite was true for azobenzene. Thus, the sensitivity toward both azobenzene and malathion increased with the ratio of sodium to boron and with rubidium concentration and, possibly, cesium concentration. In addition, a comparison of beads 2 and 3 showed that the larger bead had a somewhat greater sensitivity and improved detectability for both compounds.

The ratio of the sensitivities under conditions of equal noise is defined as the specificity (7). With the exception of the larger size Pyrex bead 3 and the cesium bead 8, the sensitivity ratio for malathion to azobenzene was always higher than that of the commercially available bead. This indicates that the beads were better phosphorus detectors than nitrogen detectors. Nevertheless, the sensitivities of our beads toward nitrogen were higher than that of the commercial bead except for bead 6 which contained no sodium. Hence, our beads were generally more specific toward phosphorus while, at the same time, more sensitive toward nitrogen than the commercial bead. However, the departures from linearity in the plots of sensitivity vs. bead currents for malathion were greater for our stabilized beads. A marked exception was noted in the freshly prepared high cesium oxide bead which showed low

malathion-azobenzene ratios, from 2.4–4.6 which means that the sensitivity toward azobenzene was 80 times greater than usual, especially when first used. However, after aging for 3 weeks, the behavior resembled that of the other beads.

For some beads, the sensitivity toward the solvent *n*-hexane was measured. The sensitivity for azobenzene and malathion was 10^6 and 10^7 larger than that for *n*-hexane. Thus, the beads had large specificities for nitrogen and phosphorus relative to hydrocarbons. The values were not significantly different, especially when one considers that they were not measured at the same bead current.

Sensitivity Studies in the P Mode. The use of the term, P mode, is deceptive in that azobenzene could usually be determined with reasonable sensitivity. The only exception was the high cesium bead, 8, which showed no sensitivity toward nitrogen in this mode. The sensitivities for azobenzene and malathion were less, except for the high rubidium bead, 7, than those obtained in the N-P mode, an observation consistent with what we have previously reported for the commercial bead 4 (6). However, the orders of sensitivity toward azobenzene and malathion were not the same in this mode. As indicated above, the cesium bead, 8, showed a low sensitivity for malathion, and it was not possible to detect azobenzene in this mode. At the other extreme the high rubidium bead, 7, showed sensitivities toward both compounds which were nearly the same in both modes.

In the P mode, the larger bead, 3, showed similar, rather low, sensitivities for both compounds whereas the smaller bead showed a higher sensitivity (and selectivity) toward malathion. When the larger bead was removed and examined under magnification, it appeared that only half of the bead had been heated by the flame because a crater appeared in the bead directly above the flame. This confirms our previous study (6) and indicates that the flame profile is important in this mode.

The data suggest that sensitivity toward nitrogen was related to the sodium content. The bead having no sodium showed low azobenzene sensitivity relative to that of malathion. Beads 2 and 6 that had the highest sensitivity ratio had the lowest amount of sodium oxide. Among the rubidium beads, those having the highest sensitivities toward both compounds had the highest rubidium concentration. Thus, in the P-mode just as in the N-P mode, high sodium and high rubidium led to high sensitivity for both compounds.

The sensitivity towards *n*-hexane, although low, was about 150–50 000 times greater in this mode. Thus, one should chromatograph under conditions where solvent tailing will not interfere with the component in question.

Detectability Studies in the N-P Mode. The beads usually fell in the same order with respect to detectability as they did for the sensitivity. The only exceptions were the reversals of beads 1 and 3 with respect to azobenzene. Bead 1, the Pyrex with sodium added, had lower detectability. There was no obvious explanation for the lower noise of the larger size Pyrex bead 3. It is worthwhile noting that, when comparing bead 4 with 6, and bead 1 with 3, the sensitivities for beads 6 and 3 were lower but their detectabilities were either higher (bead 3) or comparable (bead 6). This is a direct result of the lower noise of beads 3 and 6. Hence, larger bead size and low sodium content led to lower noise values.

Detectability Studies in the P Mode. Similar trends in sensitivities and detectabilities were observed in this mode. However, a reversal was obtained with beads 4 and 1 in their responses toward azobenzene. Although bead 1 had a higher sensitivity, bead 4 showed a higher detectability. Since the composition of the commercial bead, 4, is not known, one cannot make any correlations with composition.

Linearity. Although our method for determining the linear range was more rigorous than the conventional method, the four beads for which linearity ranges were calculated had values comparable to those reported for older versions of thermionic detectors (8, 9). The highest linear range was found for bead 7 which had the highest rubidium concentration. However, the linearity values must be used with caution because they will undoubtedly depend on the nitrogen or phosphorus compound used.

Loss of Bead Current. This is one of the most important aspects of the thermionic detector. We have previously shown how the very small changes in bead current drastically altered the reproducibility of the detector (4). If the bead current vs. heating current shifted too rapidly toward higher heating currents, continuous readjustments by the operator were required in order to achieve the best reproducibility of response. We obtained relative standard deviations of 3–6% in a 6-h period by maintaining the bead current constant.

Bead 6, the sodium-free bead, showed the highest stability, while bead 5, which had high boron and sodium contents, showed the least stability.

DISCUSSION

A high rubidium oxide concentration (10–20%), a high sodium oxide content (4–10%), and a low boron oxide content (2–3%) yielded beads having good sensitivities and detectabilities. However, a reasonably good bead could be made without sodium in contrast to what has been stated (3). While bead 6 showed very good stability and low noise, it did have lower sensitivities. It would be desirable to study beads having no sodium but a higher rubidium concentration. Those beads should have much higher sensitivities and detectabilities, the latter because of their low noise.

The presence of Al_2O_3 and K_2O was not deleterious to bead performance. In fact, bead 7 was an exceptional bead which showed larger sensitivities than the commercially available bead in both modes for azobenzene and malathion. Furthermore, its N-P and P modes did not show significant differences in behavior.

Cesium bromide and chloride have been previously used as an alkali source in thermionic detectors (8). Our bead 8 showed good sensitivity and detectability in the N-P mode but very low sensitivities in the P mode. It would be worthwhile to investigate compositions that might stabilize the bead current at 600–800 pA because, at those high bead currents, the bead showed the best azobenzene sensitivity (approximately 1.2 C/g) for azobenzene relative to malathion, a commendable property. The need for detection of phosphorus is less acute because it can also be performed using the flame photometric detector (9).

The beads were easily made in the laboratory, and they showed good sensitivities and detectabilities for nitrogen and phosphorus compounds. In addition, a new bead could easily be fused to the wire of the commercially available bead holder. The easiest beads to prepare were beads 1 and 2 because it was necessary only to add either rubidium nitrate or a mixture of the rubidium nitrate and sodium carbonate to powdered glass.

A word of caution is necessary. Our conclusions were reached using different heating currents but with otherwise identical operating conditions. From earlier studies (6), we know that operating conditions can drastically change both the sensitivity and the selectivity of a bead. Hence, one should recognize the limitations of our conclusions until detailed studies have been made under optimal conditions for each bead.

Finally, after this study had been completed, we learned that Aue and his co-workers (10) had also been successful in making beads. They confined their study to rubidium-doped

beads of quartz. Unfortunately, their results cannot be compared with ours because they studied different volatile species, and they did not characterize their beads in terms of bead current nor standardize the conditions under which they made comparative measurements. However, both their study and ours showed a higher sensitivity toward both nitrogen and phosphorus compounds for higher concentrations of rubidium in the beads.

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Microprocessor-Based, Linear Response Time Low-Pass Filter

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One of the most widely cited applications of microprocessors in scientific instrumentation is an alternative to hard-wired digital and analog circuitry. In addition to the advantages of exceptional versatility and the potential for standardization of hardware, the microprocessor approach often allows the ready implementation of functions which would be difficult to implement in hard-wired electronics. This paper describes the use of a microprocessor to implement a particularly useful type of low-pass filter, a function normally performed by analog circuitry. Although a few years ago such an application would have been quite impractical from an economic point of view, the continuing reduction in the complexity and cost of microprocessor systems and support hardware will make such an application increasingly practical in the future. More significantly for the present application, however, is that a microprocessor-based low pass filter can be designed to have uniquely desirable properties which would be difficult or impossible to achieve using conventional analog hardware. Consider for example the low-pass filter used to smooth the output signal of a flame atomic absorption spectrometer. The output signal of such an instrument (for flame atomization) is essentially a series of rectangular pulses of varying height and duration depending on the concentration and aspiration time of each sample, standard, and blank solution. Superimposed on this signal is a certain amount of random noise of white or $1/f$ spectral distribution. The objective of measurement is to determine the average height of each rectangular pulse. Low-pass filtering is commonly applied to the output signal to aid in this determination; although unnecessary if the signal is recorded on a strip-chart recorder (as then the signal may be averaged or integrated manually in various ways), low-pass filtering is often essential if a panel meter or numerical digital readout is employed. It is clearly desirable in this application to obtain the greatest noise filtering capability with the minimum response time. Long time constants, although possibly improving the signal-to-noise ratio, naturally result in long analysis times, increased sample consumption, and increased problems from long-term drift. Moreover, with graphite furnace atomization, excessively long time constants result in reduced sensitivity and greater analytical curve nonlinearity. Thus, it would seem reasonable that, if one were to compare two low-pass filters of equal

noise-filtering capability, the one with the shortest effective response time would be the best for atomic absorption applications and indeed for many other applications as well.

The most commonly used type of low-pass filter in analytical instrumentation is an active or passive single-stage RC filter, which has an exponential response to a step input. A variety of more elaborate filter types, such as Butterworth, Bessel, etc., are occasionally used for special purposes. These have different, and in some cases more efficient, response behaviors, but in many respects the ideal filter would have a linear response to a step input which would not "slow down at the end" like the RC and most other filter types. This is the response behavior of an integrator, now a standard feature on atomic absorption instruments, and in fact it is this linear response behavior which is the essential advantage of integration compared to low-pass filtering. However, the conventional integrator produces a discontinuous output signal which is unsuitable for recording spectral scans. A low-pass filter giving a continuous output signal but with the linear response of an integrator would be ideal. The closest analog approach to this ideal is the *Paynter* filter (1), a complex, third-order, linear-phase-shift active filter design employing 14 critically matched resistors and capacitors. This filter is especially useful for averaging nonstationary random variables, since its transient-response time is minimum for a given averaging time. Such a filter might be designed for any one time constant, but to make it variable would entail considerable difficulty. The microprocessor-based low-pass filter described here is an ideal linear-response time filter. It is based on a real-time modification of the sliding window algorithm widely used to smooth data arrays. Essentially, the system samples the input analog signal repetitively at some constant rate, computes the average of the *last* 2^n data points (where $0 \leq n \leq 8$) and outputs the average to a digital-to-analog converter. The response time of the filter, which depends upon the number of data points averaged, is theoretically expected to be one half that of a simple RC filter with the same noise filtering capability (2).

EXPERIMENTAL

The filter algorithm was coded for a MOS-Technology 6502 microprocessor and run on an Ebka 6502 Familiarizer (Ebka