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Studies on the Use of Colloidal Gas Aphrons in Coflotation and Solvent Sublation Processes. A Comparison with the Conventional Technique

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Abstract

The application of colloidal gas aphrons (CGA) in coflotation and solvent sublation processes has been studied. The advantages with respect to the results obtained by conventional techniques have been compared. In the solvent sublation of methyl orange with hexadecyltrimethylammonium (HTABr) in 2-octanol, yields higher than 95% are reached in 6–7 min; while in the conventional technique 20 min is necessary to obtain a little lower yield. In the coflotation of Cu with $Fe(OH)_3$ and HTABr, the separation percentage is higher than 95% in less than a minute in the absence of an induction time, which, on the contrary, amounts to 25 min in the conventional technique.

INTRODUCTION

Colloidal gas aphrons (CGA) are very small gas bubbles (average size between 25 and 100 μm) encapsulated in an aqueous-soapy film. They present some colloidal properties and can be generated from solutions of a great variety of surfactant agents (cationic, anionic, and non-ionic) which can contain up to 65% gas.

The CGA were first proposed by Sebba (*1*, *2*) under the name of microgas dispersions (MGD) or microfoams, but further experiments proved that the CGA name was more appropriate (*3*). The first CGA were obtained by Sebba using a "Venturi" generator (*1*). Sebba later developed a new way to obtain CGA in large quantities which allowed its use on an industrial scale by furnishing bubbles of a more uniform size.

The fundamental structure and properties of CGA have been studied and discussed by Sebba (*4*). From an analytical point of view, two aspects are very important: (a) small bubble size, as related to the large specific surface which can be attained; (b) the existence of a double film of the surfactant encapsulating the gas. As a consequence, important advantages relating to the use of CGA in adsorptive bubble separation processes were expected (*5*). In fact, Sebba et al. (*5–8*) have published promising results on the use of CGA in processes for the flotation of metals, dyes, unicellular algae, etc. Woodburn et al. (*9*) recently published some results on the flotation of coal particles.

Here the results of a comparative study are presented to show the advantages of using CGA in typical processes of coflotation and solvent sublation, which are well described in the literature (*10–12*), as compared with conventional separations (gas flow, etc.).

The solvent sublation of methyl orange (MO) with hexadecyltrimethylammonium bromide (HTABr) and 2-octanol has been investigated. This system was one of the first to be studied to elucidate the solvent sublation mechanism and its possibilities as an analytical separation method (*10*, *11*). In the coflotation case, the separation of traces of Cu with $Fe(OH)_3$ and HTABr was chosen; this operation has been optimized by the authors (*12–14*).

EXPERIMENTAL PROCEDURE

All the reagents used were of analytical grade.

The experiments were performed in columns which have been described elsewhere (*13*, *15*). When CGA are used, the sintered glass plate has no utility because the gas bubbles have been preformed in the CGA. Therefore, the bottom piece of the column was substituted by an identical one but without sintered glass. The evolution of the separation process (solvent sublation) of the MO was followed spectrophotometrically by taking small samples from the aqueous phase. They were acidified by adding HCl, and they were measured in a 1-cm optical path length cell in a Perkin-Elmer 575 UV-VIS spectrophotometer. The evolution of the coflotation process of Cu was controlled by measuring the residual Cu in the mother solution with a Pye-Unicam-9-800 atomic absorption spectrophotometer with an air-acetylene flame. The operating conditions were identical to those described in the literature (*12*).

A very similar system was used as a CGA generator by Sebba (*3*). A Eyela MP-3 peristaltic pump was employed to pump the CGA to the column.

MO Solvent Sublation Procedure by Means of CGA

1 mL of a 3×10^{-3} *M* aqueous solution of MO is added to 500 mL distilled water in a beaker. The pH is adjusted to 10.5 by adding NaOH, and the solution is transferred to the flotation column. 25 mL 2-octanol is placed carefully on the aqueous phase, and the CGA current is passed through (generated at that moment from a solution of 0.5 g/L HTABr) the tap at the bottom of the column. To follow the kinetics of the process, several samples of 10 mL are taken from the lateral tap. The yield is determined from the absorbance values measured at 510 nm versus distilled water.

Coflotation Procedure for Cu(II) Using $Fe(OH)_3$ and HTABr by Means of CGA

To 500 mL distilled water, add 1 mL of a solution of 1000 ppm Cu and 8 mL of a 0.05 *M* Fe(III) solution. The pH is adjusted to 10 by adding NH_3, and the whole solution is transferred into the flotation column. Through the tap at the bottom of the column the CGA (obtained from a solution of 2 g/L HTABr) is pumped at a 20 mL/min flow rate. To follow the kinetics of the process, several samples are taken at different times; once they are acidified with HCl the Cu concentration is measured by atomic absorption. The results are compared to a calibration curve created from standards of similar composition to the samples and by adjusting the experimental conditions to obtain results with a standard deviation lower than 1% (*16*).

The conventional procedures for solvent sublation of MO and for the coflotation of Cu on $Fe(OH)_3$ and HTABr are described elsewhere (*10–14*).

RESULTS AND DISCUSSION

Solvent Sublation of MO

To check the efficiency and advantages of the use of CGA in the solvent sublation of MO, it was necessary to optimize several parameters which could affect this kind of process. The parameters to be optimized were initially the concentration of the surfactant (generating agent of CGA) and its flow rate into the column.

The HTABr concentration in CGA can influence the process either as derived from the surfactant quantity added to the column or from the stability of the aphron itself. In fact, below a certain surfactant concentration limit the CGA obtained is very unstable, decomposing along the path from the beaker in which it was prepared to the column. The results obtained with aphrons prepared so that their stability ws guaranteed (surfactant concentration greater or equal to 0.1 g/L) are shown in Fig. 1. The separation of MO is greater than 90% 7 min after the

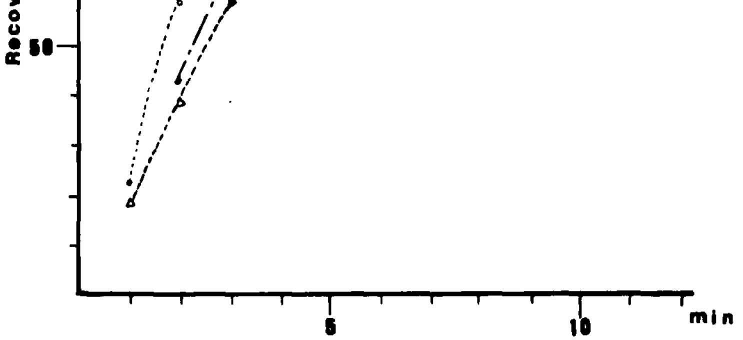

FIG. 1. Influence of HTABr concentration on the solvent sublation yield: (○) 0.5 g/L; (●) 0.2 g/L; (△) 0.1 g/L; V_{aq} = 500 mL; V_{or} = 25 mL; pH = 10.5; CGA flow = 30 mL/min.

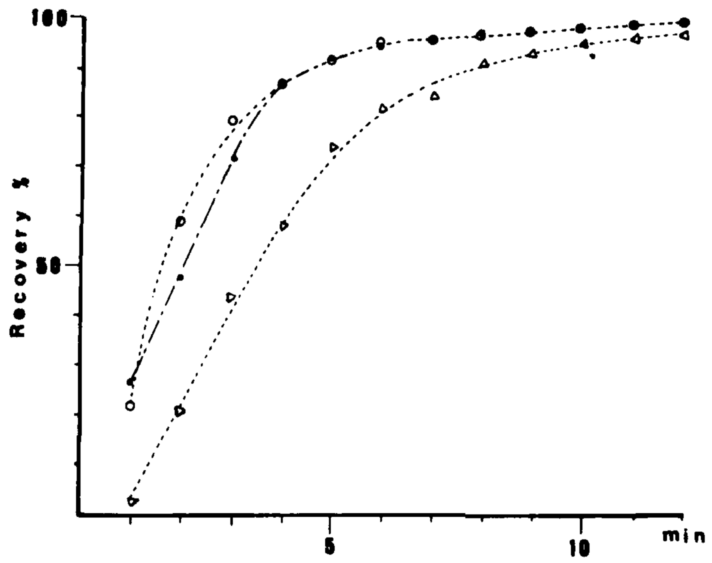

FIG. 2. Influence of CGA flow rate on the solvent sublation yield: (○) 30 mL/min; (●) 20 mL/min; (△) 10 mL/min; V_{aq} = 500 mL; V_{or} = 25 mL; pH = 10.5; [HTABr] = 0.5 g/L.

process is started, and the best results are obtained when the concentration of HTABr is 0.5 g/L.

The pump flow of CGA to the column can affect the process because it is a measure of the quantity of surfactant added to the column. On the other hand, this is a measure of the gas flow to the column, and this is one of the variables that concerns solvent sublation processes in general.

Therefore, several experiments were carried out by varying the CGA flow to the column. From the results of Fig. 2 it is concluded that, for a flow greater or equal to 20 mL/min, separation is satisfactory (yield higher than 90% in 6–7 min of flow current of CGA).

In Fig. 2 it is observed that the kinetics of the process is slower for a pumping velocity of about 10 mL/min. However, the quantity of gas flowing into the column is not the only factor to take into account. In fact, the residence time of CGA in the conduction pipe to the column is inversely proportional to that velocity. When the pump velocity is small, considerable damage in its structure can occur. In Fig. 3 the results are shown for aphrons obtained from 0.1 g/L HTABr pumped at 20 or 30 mL/min to the column, and it is seen that the separation yield does not decrease significantly but the kinetics of the process becomes much slower.

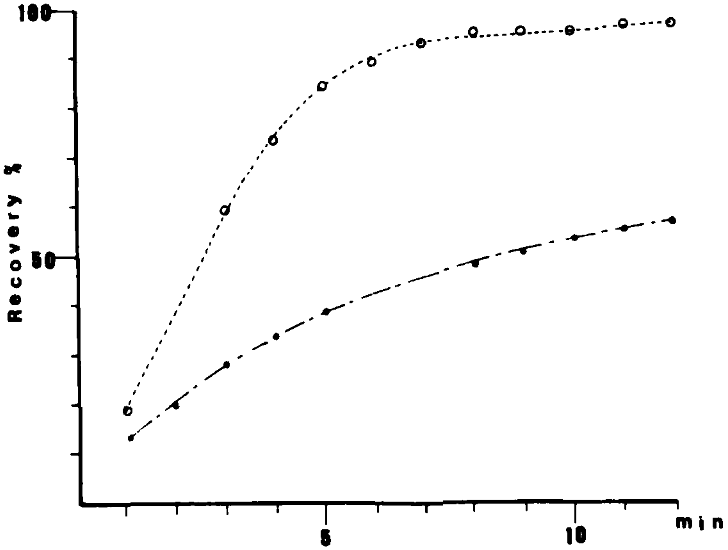

FIG. 3. Influence of HTABr concentration on the kinetics of solvent sublation process and the CGA stability: (O) 30 mL/min; (●) 20 mL/min; V_{aq} = 500 mL; V_{or} = 25 mL; pH = 10.5; [HTABr] = 0.1 g/L.

Therefore, the two main factors to take into account in these processes are: (a) the minimum concentration of surfactant, and (b) CGA flow to the column, which must be established in such a way that the CGA will reach the column without any structural damage.

Volume of 2-Octanol

Finally, some other experiments were performed by varying the amount of 2-octanol, maintaining the other parameters constant, in order to check one of the fundamental properties of solvent sublation: the quantity of separated species is independent of the volume ratio in both phases (except for the case in which the organic phase becomes saturated by the species to be separated). The results of Fig. 4 show that, as in the above cases, the separation of MO is greater than 90% after 6–7 min, and it is almost independent of the 2-octanol volume.

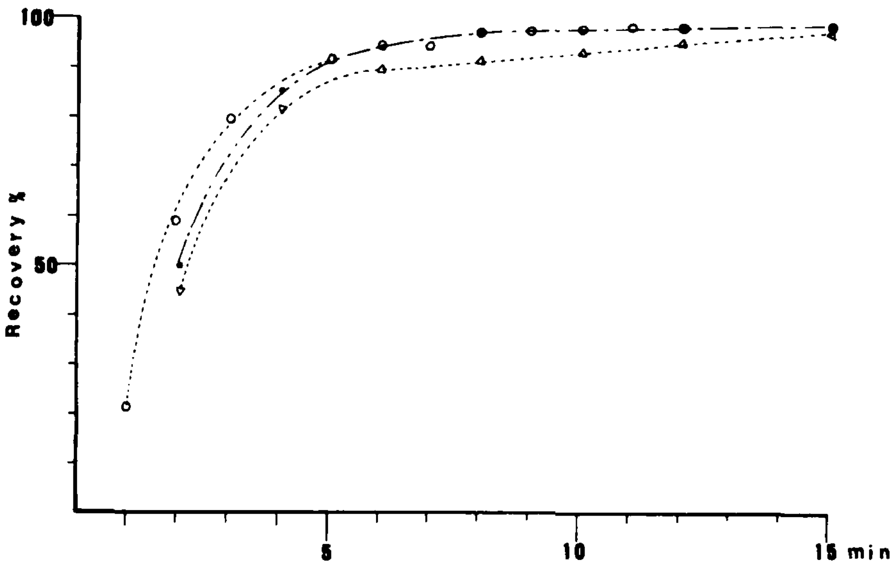

FIG. 4. Influence of 2-octanol volume on the solvent sublation yield: (△) 10 mL; (●) 25 mL; (O) 50 mL; V_{aq} = 500 mL; pH = 10.5; CGA flow = 30 mL/min; [HTABr] = 0.5 g/L.

Volume of Sample

One of the main advantages of the solvent sublation technique is the possibility of handling large sample volumes easily. Joining this to the nonexistence of a real partition equilibrium, large preconcentration factors can be obtained. However, when it is attempted to reproduce this kind of process as described in the literature, it is necessary to modify some experimental parameters (surfactant quantity, gas flow) when the sample volume is changed. In order to study the need to adjust the experimental conditions to use CGA, several experiments were carried out with 0.5, 1, 2, and 5 L samples. In all cases the experimental conditions were strictly fixed. The results obtained are presented in Fig. 5. For 0.5 and 1 L there are no apparent differences. The kinetics becomes a little slower for a 5-L sample because the column is longer and therefore the CGA take more time to reach the organic phase.

On the other hand, Karger's et al. studies (*10*, *11*) on the solvent sublation of MO indicate that at least 20 min was necessary to obtain

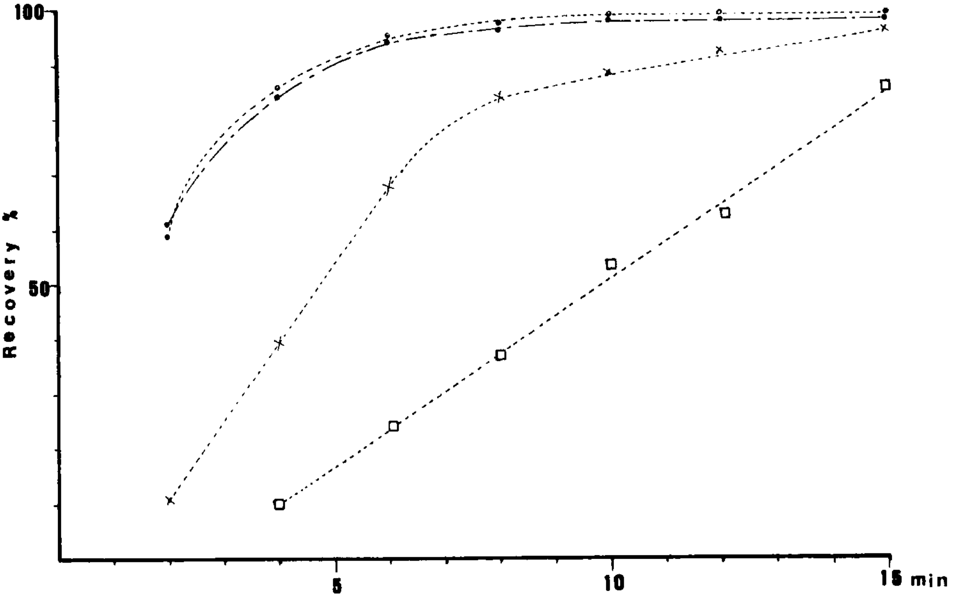

FIG. 5. Effect of sample volume on the solvent sublation yield and kinetics: (□) 5 L; (×) 2 L; (O) 1 L; (●) 0.5 L; V_{0r} = 25 mL; pH = 10.5; CGA flow = 30 mL/min; [HTABr] = 0.5 g/L.

separations with yields of less than 90%. Greater yields can be easily obtained by using CGA in 6–7 min, thus reducing dramatically the overall time of the process, which is the principal inconvenience of the solvent sublation technique when it is used for practical purposes.

Coflotation of Cu with Fe(OH)$_3$ and HTABr

The main optimized and controlled parameters in this process are:

Quantity of coprecipitant species
Passing time of CGA flow
pH of the medium
Flow of CGA at the entrance of the column
HTABr concentration of the initial solution in the CGA obtention
Induction time

Quantity of Coprecipitant Species

According to the most favorable results obtained by coflotation (*12*), several experiments were performed by varying the quantities of 0.05 *M* Fe(III) solution at pH = 10 with a CGA flow of 30 mL/min for 1 min. The results are presented in Fig. 6(a) which shows that between 6 and 10 mL Fe(III) yields a separation above 95% in just 1 min. From these results 8 mL of 0.05 *M* Fe(III) was chosen as the optimum coprecipitant quantity.

Passing Time of the CGA Flow

To know the exact influence of this parameter, several experiments were performed using 8 mL Fe(III). The results are shown in Fig. 6(b), from which it can be appreciated that 1 min is enough time to reach 95% separation. It is obvious taht once the flow of CGA is stopped, the microbubbles need time to reach the liquid surface. All the data in this work refer to the time until the CGA flow is stopped, and therefore the solution is still cloudy. However, there is not much difference between this situation and waiting for a completely clear solution. The data of Table 1 confirm this statement.

pH of the Medium

These results are shown in Fig. 6(c). There is a wide range of pH values for which the separation is greater than 90% (between 7.5 and 12) and a narrower neighborhood (between 8 and 10) where a 95% separation can be achieved. From the kinetic results it is deduced that the process proceeds quickest between pH 9.5–11; therefore, pH 10 was chosen as the optimum for the process.

CGA Flow

For similar reasons as in the case of solvent sublation, several experiments were performed to determine the optimum flow of CGA in the column. The influence of this parameter is shown in Fig. 6(d). A separation superior to 95% was obtained for flow rates between 10 to 30

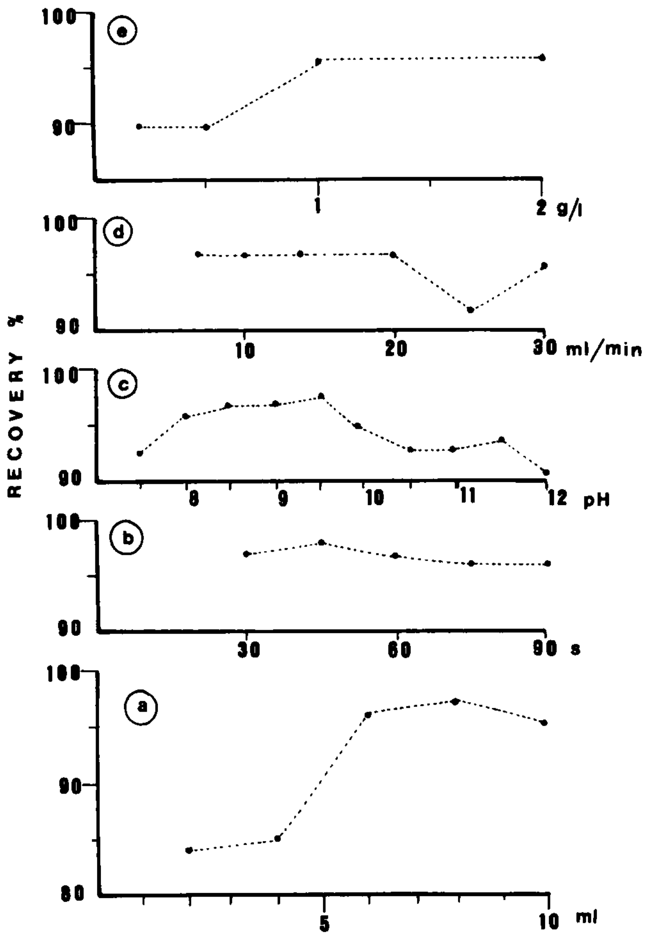

FIG. 6. Influence of experimental variables on the CGA coflotation of Cu(II). (a) Amount of Fe(III) coprecipitant. (b) Passing time of the CGA flow. (c) pH of the mother solution. (d) CGA flow rate. (e) HTABr concentration in the CGA.

mL/min. To avoid damaging the CGA structure in the column, a 20-mL/min working flow rate was chosen.

HTABr Concentration

With the above parameters fixed, several experiments were performed by varying the surfactant concentration in the solution which generates

TABLE 1
Separation Yields Obtained by Means of CGA as a Function of Time

CGA passing time (s)	Separation yield (%) at the moment of stopping the CGA flow	Separation yield (%) when the mother solution becomes clear
30	95	97
45	98	98
60	97	97
75	97	96
90	96	96

the aphron. The results obtained appear in Fig. 6(e). Based on these data, a 2-g/L HTABr concentration was chosen to generate CGA.

Induction Time Influence

In the conventional coflotation method it is necessary to maintain the stirred solution with the iron hydroxide formed (induction time during a period of about 25 min) in order to reach a 95% flotation yield (*12*). All the data presented here with CGA were obtained without any induction time. Therefore, in all these processes the induction time has no influence. Nevertheless, some experiments were performed with various induction times, but the results did not improve the yield. On the contrary, a small decrease in the separation percentage of Cu was noted.

Comparison of the Conventional Technique and CGA

From the results obtained it is concluded that using CGA noticeably improves Cu separation because no induction time is necessary and the process is faster (just 1 min). On the other hand, when the porous plate is removed from the coflotation device the quantitative recovery and the cleaning of the column is easy and accurate. Table 2 sums up the main characteristics and differences evidenced between separation by coflotation of Cu using the conventional technique and CGA.

TABLE 2
Comparison between Conventional and CGA Coflotation Processes

	Technique	
	Conventional (*12*)	CGA
Induction time	25 min	Not necessary
Coflotation time	5 min	1 min
% Separation	97 ± 2	96 ± 1

CONCLUSIONS

The above experiments show that CGA are highly effective in flotation processes by substituting the flow current of air or gas and the addition of surfactant to the solution. In the processes studied, separation yields even higher than those obtained by conventional flotation or solvent sublation techniques were obtained, and the kinetics of the process proved to be much more favorable. For these reasons, it is hoped that CGA can improve considerably the efficiency of separation processes using the flotation techniques and their applications both in analytical chemistry and other fields.

REFERENCES

1. F. Sebba, *J. Colloid Interface Sci., 35,* 643 (1971).
2. F. Sebba, U.S. Patent 3,900,420 (August 1975).
3. F. Sebba, *Chem. Ind., 4,* 91 (1985).
4. F. Sebba, *Investigation of the Modes of Contaminant Capture in CGA (MGD) Foams,* Office of Water Research and Technology, Washington, D.C., 1981, OWRT/RU-82/10.
5. F. Sebba, *Sep. Purif. Methods, 14,* 127 (1985).
6. P. T. Shea and S. M. Barnett, *Sep. Sci. Technol., 14,* 757 (1979).
7. S. Ciriello, S. M. Barnett, and F. J. DeLuisse, *Ibid., 17,* 521 (1982).
8. D. A. Wallis, D. L. Michelsen, F. Sebba, J. K. Carpenter, and D. Houle, *Biotechnol. Bioeng. Symp., 15,* 399 (1986).
9. E. T. Woodburn, D. J. Robbins, and J. B. Stockton, *Filtr. Sep., 24,* 89 (1987).
10. B. L. Karger, A. B. Caragay, and S. B. Lee, *Se. Sci., 2,* 39 (1967).
11. B. L. Karger, T. A. Pinfold, and S. E. Palmer, *Ibid., 5,* 603 (1970).
12. L. M. Cabezón, R. Cela, and J. A. Pérez-Bustamante, *Afinidad, 40,* 144 (1983).
13. R. Cela and J. A. Pérez-Bustamante, *Ibid., 39,* 107 (1982).
14. M. Caballero, R. Cela, and J. A. Pérez-Bustamante, *Sep. Sci. Technol., 21,* 39 (1986).
15. J. Cervera, R. Cela, and J. A. Pérez-Bustamante, *Analyst, 107,* 1425 (1982).
16. Pye-Unicam SP-9-Series A.A.S., *Users Manual,* Pye-Unicam Ltd., Cambridge, England.

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