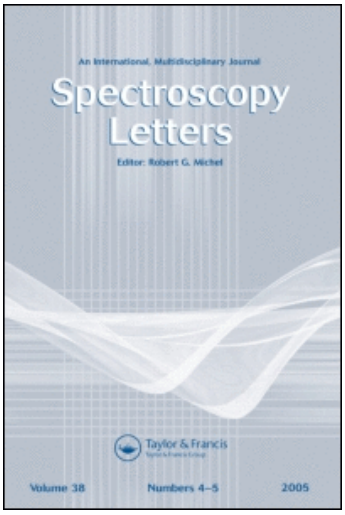

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Green Chemistry–Sensitive Analytical Procedure for Photometric Determination of Orthophosphate in River and Tap Water by Use of a Simple LED-Based Photometer

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An invited paper submitted to a special issue on Green Spectroscopy and Analytical Techniques, organized by Professor Miguel de la Guardia, of the Department of Chemistry, University of Valencia, Spain, and Professor Arabinda Kumar Das, of the Department of Chemistry, University of Burdwan, West Bengal, India.

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ABSTRACT In the current work a Green Analytical Chemistry (GAC) procedure for photometric determination of orthophosphate in river water at $\mu g\,L^{-1}$ concentration level is described. The flow system module and the LED-based photometer were assembled together to constitute a compact unit in order to allow that a flow cell with optical path-length of 100 mm was coupled to them. The photometric procedure based on the molybdenum blue method was implemented employing the multicommuted flow injection analysis approach, which provided facilities to allow reduction of reagent consumption and as well as waste generation. Aiming to prove the usefulness of the system, orthophosphate in river and tap waters was determined. Accuracy was ascertained by spiking samples with orthophosphate solution yielding recoveries ranging from 96% up to 107%. Other profitable features such as a wide linear response range between 10 to 800 $\mu g\,L^{-1}$ PO_4^{3-}; a detection limit (3σ criterion) of 2.4 $\mu g\,L^{-1}$ PO_4^{3-}; a relative standard deviation ($n = 7$) of 2% using a typical water sample with concentration of 120 $\mu g\,L^{-1}$ PO_4^{3-}; reagent consumption of 3.0 mg ammonium molybdate, 0.3 mg hydrazine sulfate, and 0.03 mg stannous chloride per determination; a waste generation of 2.4 mL per determination; and a sampling throughput of 20 determination per hours were also achieved.

KEYWORDS LED-based photometer, long pathlength flow cell, multicommuted flow injection analysis, orthophosphate and water, spectrophotometry

INTRODUCTION

Environmental preservation became an actual paradigm and in this context attention has been given to prevent pollution of water sources. The intensive use of water increases its contamination risk, therefore the potential polluting chemical species must be monitored to access the quality of

water. The analytical procedures employed to accomplish this proposal could use hazardous reagents, thus generating also waste that could become a polluting agent. To overcome this drawback the use of methods based on the Green Analytical Chemistry (GAC) concept has been suggested.[1–3] The availability of reliable analytical procedures presenting robustness, sensitivity, and accuracy maintaining accordance with the GAC concept is an ideal to be attained and its development a challenge to be faced today.

The multicommuted flow injection analysis (MCFIA) is a tool that has been employed to accomplish the subject concerning reduction of reagent consumption as well as waste generation.[4,5] A flow system based on the MCFIA process comprised a set of solenoid valves, each one assembled to work as an independent commuting device controlled by a personal computer, which enabled them to deliver aliquots of sample and reagent solution into the reaction coil. These facilities have been employed to develop environmentally friendly analytical procedures focused on reduction of waste.[6,7]

Orthophosphate is considered a polluting agent that contributes strongly for the eutrophication of the natural waters.[8–10] Industrial and agricultural activities as well as domestic sewage are considered the main delivering sources.[11–13] In this sense, a Brazilian governmental agency[14] established that for drinking water 20 $\mu g\,L^{-1}$ PO_4^{3-} must be the maximum acceptable concentration. This concentration is very low, thus it is necessary to use a high sensitivity analytical procedure. Procedures based on flow injection analysis using stopped flow,[15] solid phase enrichment,[16] and pre-concentration with ion exchange resin[17] have been employed to improve sensitivity, nevertheless, reduction of waste was not considered.

In the Green Analytical Chemistry (GAC) context high sensitivity analytical procedures as well as portable equipment setup could be also considered requirements to be attained. Liquid core waveguide flow cell presenting optical pathlength of 100 cm has been employed to improve sensitivity in flow injection system,[18–20] while portable photometers have been designed using LED as a radiation source.[21,22]

Analytical procedures based on multicommuted flow injection analysis (MCFIA) have been implemented positioning the peristaltic pump either between the detection setup and the waste vessel, or positioning them between the solutions vessels and reaction coil.[7] In the first case, solutions are displaced through the analytical path by suction (puling mode) using a single pumping channel. In the second one (pushing mode), solutions are displaced, propelling them using a pumping channel for each solution. Commuting the solenoid valves the solutions are displaced either through the analytical path toward the detector or to back their storing vessels.

In this work, we intend to develop a downsized equipment setup combining a MCFIA manifold and a LED-based photometer to form a compact unit with facilities to implement an analytical procedure according to the GAC requirement, which will be employed for the photometric determination of orthophosphate in water employing the molybdenum blue method.[15] The system will be designed to work employing both pulling mode and pushing mode, thus solutions inserting into analytical path will be performed using a single pumping channel, while the displacement through the analytical path will be carry out by propelling them to prevent gas delivering into sample bulk. Considering that the sensitivity of the analytical procedure must be enough to attain the regulatory requirements, the flow system and the photometer will be designed to allow that a flow cell with an optical pathlength of 100 mm could be coupled to them.

EXPERIMENTAL

Reagents

All chemicals were of analytical grade. Purified water with electric conductivity less than 0.1 $\mu S\,cm^{-1}$ was used throughout.

Ammonium molybdate solutions (1.0%, w/v) in 0.6 $mol\,L^{-1}$ H_2SO_4 medium was prepared by dissolving 5.00 g of solid in 50 mL of water. After dissolution a volume of 16.5 mL concentrated H_2SO_4 was added to the vessel and the volume was made up to 500 mL with water. Stannous chloride solution (0.02%, w/v) plus hydrazine sulfate (0.2%, w/v) in 0.5 $mol\,L^{-1}$ H_2SO_4 solution was prepared by dissolving the solids each one in 50 mL of water. After dissolution both solutions were transferred to a 500 mL flask, 14 mL of concentrated H_2SO_4 was added to the vessel and volume was made up to 500 ml with water. Tartaric acid solution (1%, w/v) was prepared

dissolving 5 g in 500 mL of water. A 1000 mg L^{-1} PO_4^{3-} stock solution was prepared by dissolving 0.7168 g of KH_2PO_4 in water and after dissolution the volume was make up to 500 mL. This solution was maintained in refrigerator. Working standard solutions with concentrations of 0.0, 10.0, 25.0, 50.0, 100.0, 200.0, 400.0, 600.0, and 800.0 μg L^{-1} PO_4^{3-} in 0.014 mol L^{-1} HNO_3 medium were prepared daily using a 10 mg L^{-1} PO_4^{3-} solution, which was prepared by appropriated dilution with water from the stock solution.

Water samples were collected at different point of Piracicaba and Corumbataí rivers, which were filtered and processed in the same day. Tap water was also collected and analyzed in the same day.

Apparatus

The equipment setup comprised three pinch solenoid valves normally closed (161P011), one pinch solenoid valve normally open (161P021), and one three-way solenoid valve (161T031) purchased from Nresearch (West Caldwell, NJ); an IPC4 Ismatec (Switzerland) peristaltic pump furnished with Tygon pumping tubes; a Pentium IV microcomputer equipped with an interface card (PCL711 S, Advantech Corp.); a power supply (12 V) to feed the solenoid valves; reaction coils and flow lines made of polyethylene tubing (0.8 mm i.d.); joint device machined in acrylic; a homemade electronic interface to drive the solenoid valves, which was wired as described elsewhere.[6] The photometer comprised a red LED ($\lambda = 640$ nm, high bright and narrow radiation beam) and a photodiode IPL10530DAL (RS Components). A flow cell with a 100 mm optical path-length at *Z* format was constructed using a borosilicate glass tube with 2.0 mm inner diameter. The observation windows at the *Z*-corners aligned with the flow cell optical pathway were molded to form plane surfaces (≈3 mm^2); two metallic plates, 4.0 cm long, 2.0 cm wide, and 2.0 mm thickness with central holes with 1.8 mm diameter. The control of the flow system and data acquisition were carried out by the microcomputer running a software written in Quick BASIC 4.5.

Flow System Assembling and Procedure

The diagram of the flow system is shown in Fig. 1. In this configuration all valves are switched OFF, carrier solution (Cs) flows though valve V_1 aspirated by the peristaltic pump (Pp), and propelled toward waste (W). The holes of the metallic plates (Mp) were aligned to the observation windows of the flow cell to serve as light collimator.

When the software was run, the microcomputer requested the photometer calibration, which was done turning OFF the LED to read the dark signal (Ds). Afterward, the LED was powered turning forward the variable resistor wired to base of the transistor (Tr).The output signal (S_0) was adjusted to 2000 mV. The measurements Ds and S_0 were saved as references, which were used for the absorbance calculation.

After calibration step, standard solutions or samples were processed running the system as depicted in the valves timing course of Fig. 1, which was done by the microcomputer sending through the digital interface[6] a set of control signal to switch ON/OFF the solenoid valves, which was done following the depicted switching pattern. The valves timing course shows that valves V_1, V_2, V_3, and V_4 were sequentially switched ON/OFF to insert into the analytical path slugs of sample (S), reagents solutions (R_1, R_2). A V_1, V_2, V_3, and V_4 switching sequence is named a sampling cycle (Sc), which can be repeated several times to load the analytical path with slugs of sample and reagent solutions. While valves V_2, V_3, and V_4 were sequentially switched ON, the carrier stream (Cs) was halted. As we can see, prior to beginning the next sampling cycle, valve V_1 was switched OFF during a time interval of 0.5 s to insert a slug of tartaric acid solution (Cs), which was used to suppress interference that could be caused by silicate. After the sampling step all valves were maintained switched OFF, thus the carrier solution (Cs) flowed to displace the sample zone toward the flow cell (Fc). The mixing between sample and reagent solution slugs, as well as the chemical reaction, proceeded while sample zone was displaced through the reaction coil (B_1). The analytical signal (Sg) was read by the microcomputer through the analog input of the PCL711 s interface card. After the signal reading step (Rs) valve V_5 was switched ON to empty the flow cell.

As shown in the flow diagram, the insertion of sample and reagent solutions slugs were controlled by mean of the valves V_1, V_2, and V_3, thus the volume of sample zone was controlled by varying the number of sampling cycles (Sc). The assays to find the best operational conditions were carried out by settling the time interval to maintain valve

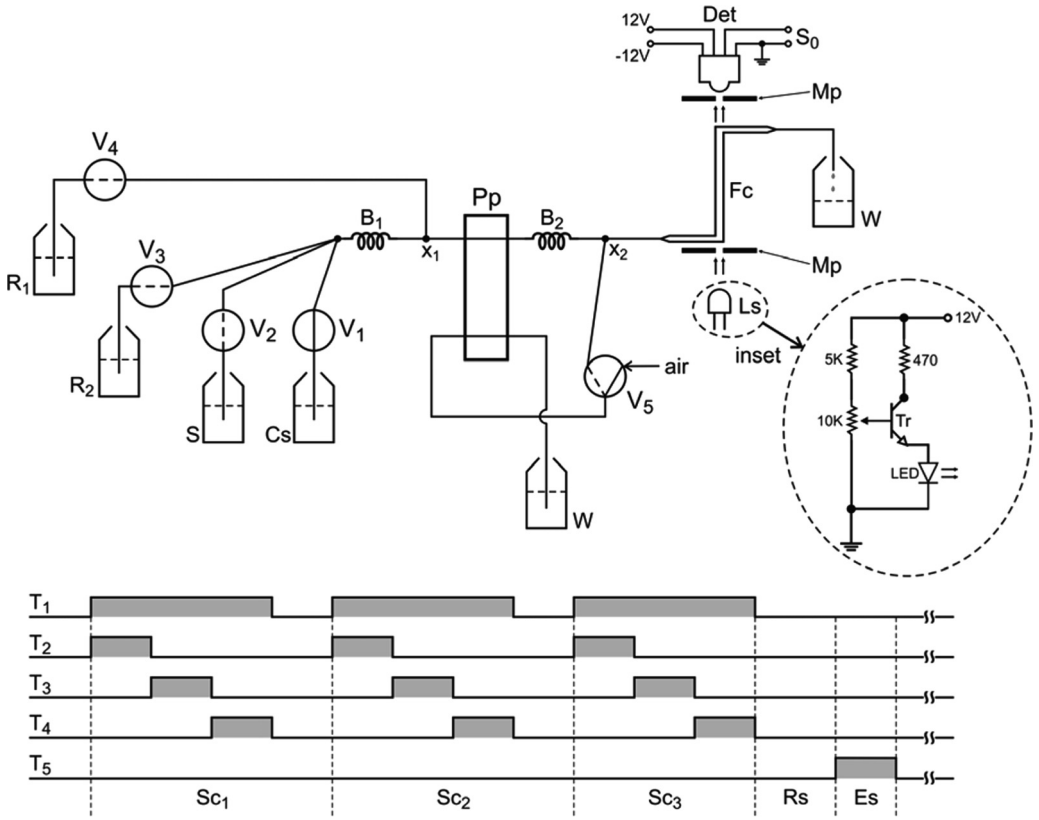

FIGURE 1 Diagram of the flow system and of the photometric detector. V_1 = pinch solenoid valve normally open; V_2, V_3, and V_4 = pinch solenoid valve normally closed, V_5 = three-way solenoid valve; B_1 and B_2 = reaction coils 15 and 25 cm length, respectively; Cs = tartaric acid solution, flow rates of 20 $\mu L\,s^{-1}$; air = air stream, flow of 50 $\mu L\,s^{-1}$; S = sample or standard solution; R_1 and R_2 = ammonium molybdate and stannous chloride solutions plus hydrazine sulfate, respectively; x and y = confluence points; Pp = peristaltic pump; Det = photodetector, IPL 10530 DAL; S_0 = signal output (mV); Fc = flow cell; W = waste; Ls = light source, red LED, λ = 660 nm and Tr = transistor BC547; Mp = metal plates (brass) 2 mm thickness, each one with a central hole, 1.8 mm inner diameter, aligned with the radiation beam. Solid lines into the symbols of valves indicate that solutions flow through them while maintained switch OFF and dashed lines indicate that solutions propelling through them were permitted only when they were switched ON. T_1, T_2, T_3, T_4, and T_5 = timing course to switch ON/OFF valves V_1, V_2, V_3, V_4, and V_5, respectively. The shadow surfaces beneath of lines indicate that the corresponding valve was switched ON. Sc_1, Sc_2, and Sc_3 = sampling cycles; Rs = signal reading step; Es = flow cell empting step. The arrows indicate the propelling direction. Reactions coils and flow lines were of polyethylene tubing 0.8 mm inner diameter.

V_2 switched ON at 1.0 s and varying from 0.2 up to 1.2 s the time intervals to maintain valves V_3 and V_4 switched ON. These assays were carried out employing 20 sampling cycles (Sc_1+Sc_2+Sc_3 +. . .). Afterward, the time intervals to switched ON V_2, V_3, and V_4 were maintained at 1.0, 0.5 and 0.5 s, respectively, and the number of sampling cycles, was varied from 10 up to 25. These experiments were carried out using a set of orthophosphate standard solution with concentration within the range of 10 to 800 $\mu g\,L^{-1}$.

Intending to prove the usefulness of the proposed system for the determination of orthophosphate, samples of river water and tap water were analyzed using the parameters depicted in Table 1. Aiming accuracy assessment samples were spiked with an orthophosphate standard solution, which were processed employing the same operational condition.

TABLE 1 Flow System Control Parameters

Step	V_1	V_2	V_3	V_4	V_5	Duration (s)	Repetition
Inserting sample	1	1	0	0	0	1.0	15
Inserting R_1	1	0	1	0	0	0.5	15
Inserting R_2	1	0	0	1	0	0.5	15
Inserting Cs	0	0	0	0	0	0.5	15
Signal reading	0	0	0	0	0	50	1
Flow cell empting	0	0	0	0	1	10.0	1

RESULTS AND DISCUSSION

General Comments

In this article attention was paid to develop a downsized equipment setup to implement an environmentally friendly and high sensitivity analytical procedure for photometric determination of orthophosphate

in water. In order to attain this objective, the flow system and the photometer were designed to allow that a flow cell with optical pathlength of 100 mm was coupled to them, which became feasible using as radiation source a LED presenting a high intense and narrow radiation beam.

It would be expected that light reflection and Schlieren effect could impair the use of the flow cell with long optical path. In the first case, the effect was minimized employing a flow cell molded with plane surfaces (windows) for light input and output and a collimation arrangement for the radiation beam (see Fig. 1). As radiation source it cemployed a LED that emitted a high intense and narrow radiation beam, thus permitting to select the full scale (2000 mV) without any additional amplification stage.

In earlier work it was pointed out that Schlieren effect prevails under poor mixing condition.[23] The authors emphasized that it becomes less pronounced as the mixing conditions are improved. In the present work, the profiles of the signals generated does not shown abrupt variations related to front edges of sample zone, that is inherent to Schlieren effect. In Fig. 1 it was shown that sample zone merged into the analytical path at the joint device (x_2). The sample zone was displaced toward the detector though the Tygon pumping tube with inner diameter of 1.0 mm and length of 250 mm. Its inner volume was 200 μL, thus allowing a primary mixing step between sample and reagent solutions slugs. Under this condition, we could expect that the peristaltic movement improved the mixing between slugs of sample and reagent solutions, thus preventing the Schlieren effect.

Generally in flow injection system the carrier solution is the main contributor to generate waste, which could be considered as a disadvantage according to the Green Analytical Chemistry (GAC) concept. In the present work, the waste volume was reduced by empting the flow cell after the signal reading step, which was done maintaining valve V_5 (Fig. 1) switched ON during a time interval of 10 s. If this step was not employed, a time interval of 40 s was required to wash the flow cell, thus delivering to waste 600 μL of the carrier solution.

Air bubbles accumulating in the corners has been pointed out as a limitation concerning the use of the *Z*-format flow cell.[24] The flow cell (Fig. 1) was installed at the vertical position thus avoiding air bubbles entrapment, therefore the flow cell could be empty after each analytical run and filled again with carrier solution maintaining the optical pathway without air bubbles.

When sample or standard solution was processed, the signal generated by photometer (Sg) was lower than the full scale value (S_0). The absorbance was derived using the relationship $A = -\mathrm{Log}[(Sg - Ds)/(S_0 - Ds)]$, which was saved as an ASCII file to allow further processing. The dark measurement (Ds) and S_0 (2000 mV) were established at the experimental section. While the sample processing was in course, a plot of the signal was displayed on the microcomputer screen as a time function to allow its visualization at real time.

Flow System Variable Optimization

The time interval to maintain valve V_2 switched ON was settled at 1.0 s, since the flow rate was kept at 20.0 μL s^{-1}, the volume of sample slug inserted per sampling cycle (Sc) was 20.0 μL. The time intervals to maintain switched ON valves V_3 and V_4 were varied from 0.2 up to 1.2 s, therefore the volumes of the solution slugs varied from 4.0 up to 24.0 μL. As it was shown in the valves timing course (Fig. 1), prior to begin a new sampling cycle valve V_1 was maintained switched OFF during a time interval of 0.5 s to insert into reaction coil (B_1) 10 μL of tartaric acid solution (Cs) to suppress silicate interference. These experiments were carried out using a set of orthophosphate standard solution with concentration ranging from 10 up to 800 μg L^{-1}. Taking peak height as the measurements parameter, liner responses ($R = 0.999$) were observed for all assays, nevertheless better sensitivity [slope $= (1.3412 \pm 0.0123)$ L μg^{-1}] was achieved when volumes of both reagents solution slugs were between the range of 8.0 to 16.0 μL. Considering these results, the time intervals to maintain valves V_3 and V_4 switched ON during a sampling cycle were settled at 0.5 s to insert slugs of solutions with volume of 10 μL, thus maintaining a compromise between sensitivity and saving of reagents solutions.

Considering that volume of sample zone can affect both sensitivity and throughput, a set of experiments was carried out in order to select the better condition, which was done by varying the number of sampling cycles from 10 up to 25. Each set of results presented linear relationship, nevertheless the slope related to experiments performed employing 10

sampling cycles was less than those achieved employing the other ones. The values of the slopes were $(1.3274 \pm 0.0141)\text{L}\,\mu\text{g}^{-1}$, $(1.3412 \pm 0.0123)\text{L}\,\mu\text{g}^{-1}$, and $(1.3451 \pm 0.0153)\text{L}\,\mu\text{g}^{-1}$ for 15, 20, and 25 sampling cycles, respectively. Since the difference was less than 2%, it was considered not significant, therefore 15 sampling cycles was selected. Considering that the time intervals to maintain switched ON valves V_2, V_3, and V_4 to perform a sampling cycle were settled at 1.0, 0.5, and 0.5 s, respectively, the volume of sample zone for the further experiments was maintained at 600 μL

Sample Analysis and Figures of Merit

Samples of river water and tap water were analyzed to prove the usefulness of the proposed system. To allow Accuracy, assessment samples were spiked with an orthophosphate standard solution. Results derived taking peak height as the measurement parameter are shown in Table 2, where we can see that recovery within range of 96 to 107 were obtained, which could be considered acceptable.

The figure of merit of the proposed system is shown in Table 3, where we can observe that its performance is comparable with those presented in the literature.[19] As we can see, the throughput was equal, but reagent consumption and waste generated were less than those observed in the referred paper. The analytical curve comprise a concentration range between 10 up to 800 $\mu\text{g}\,\text{L}^{-1}$, therefore the proposed procedure is enough to accomplish the regulatory requirement,[14] which consider 20 $\mu\text{g}\,\text{L}^{-1}$ the acceptable concentration of orthophosphate in tap water.

TABLE 2 Results of Water Analysis and Recoveries

Sample	Concentration PO_4^{3-} ($\mu\text{g}\,\text{L}^{-1}$)	Spiked PO_4^{3-} ($\mu\text{g}\,\text{L}^{-1}$)	Found PO_4^{3-} ($\mu\text{g}\,\text{L}^{-1}$)	Recovery (%)
1*	189.7 ± 3.8	200	214.2 ± 4.5	107.1
2*	159.5 ± 3.4	200	208.7 ± 5.6	104.3
3*	190.3 ± 4.7	200	212.4 ± 2.7	106.2
4**	131.9 ± 3.9	100	106.1 ± 1.9	106.5
5*	85.5 ± 1.3	100	103.9 ± 2.3	103.3
6**	83.2 ± 2.1	100	103.3 ± 2.1	103.3
7**	141.4 ± 4.2	100	171.4 ± 5.3	106.7
8**	224.1 ± 7.5	100	96.5 ± 1.3	96.2
9**	—	25	24.1 ± 0.6	96.0
10***	—	25	24.6 ± 0.3	98.0
11***	—	25	25.3 ± 0.5	101.1
12***	—	25	24.2 ± 0.1	96.8

Results are average of three replicates. *, **, and *** = water samples of Piracicaba River, Curumbataí River, and tap water, respectively. The trace notation indicates that the orthophosphate was not detected.

TABLE 3 Figures of Merit

Parameters	Ref. 19	Proposed procedure
Linear range ($\mu\text{g}\,\text{L}^{-1}$)	0.95–95	10–800
Regression coeficiente (R^2)	0.9986	0.9997
Slope ($\text{L}\,\mu\text{g}^{-1}$)	0.7264	1.3274
Blank standard deviation ($\mu\text{g}\,\text{L}^{-1}$)	—	0.6
Limit of detection, criterion 3σ ($\mu\text{g}\,\text{L}^{-1}$)	0.9	1.4
Ammonium molybdate consumption (R_1) (mg)*	7.2	3.0
Stannous chloride consumption (R_2) (mg)*	0.14	0.03
Hydrazine sulphate consumption (R_2) (mg)*	1.4	0.3
Sample throughput per hours	25	25
Waste (mL)**	4.3	2.4

The notations * and ** correspond to consumption and waste generated per determination, respectively.

CONCLUSION

Considering the results obtained we can conclude that the proposed system attained the Green Analytical Chemistry (GAC) requirement, comprising also as profitable features high sensitive and long-term stability.

The equipment setup including the flow system module, the photometer and power supply weight less than 2 kg and was housed in a little box, thus providing the portability requisite.

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