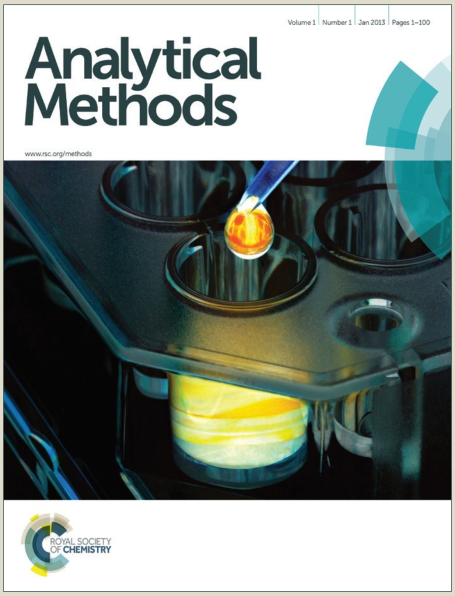

Multilayer and multichannel membrane filtration for separation and preconcentration of trace analytes and its application in spectral analysis

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Abstract:

Membrane filtration (Microfiltration) as a solid-phase extraction technique with features of rapidity, simplicity of operation, low cost, and high enrichment efficiency has received considerable attention and has been widely used for separating and enriching analytes from fluids. On the basis of our previous research, a very simple but effective mode of multilayer membrane filtration-enrichment process was introduced into the case of quantitative detecting two or more analytes in mixture samples to achieve the target of separating and concentrating analytes simultaneously.

A case study was carried out to assess this method utilizing the carcinogenic dyes rhodamine B (RhB) and acid orange 7 as model analytes. Under the optimal conditions, linearity of calibration curve based on the Kubelka-Munk function was achieved in the concentration range of 3-30 μg L-1 with the correlation coefficients (R2) of 0.9982 and 0.9952 for RhB and acid orange 7, respectively. Good repeatability was achieved utilizing 30, 10 and 5 μg L-1 solutions with the relative standard deviations (RSD) were 3.1%-6.4% for RhB and 2.4%-5.8% for acid orange 7, respectively. The presented method was successfully employed to simultaneously quantify RhB and acid orange 7 in soft drink and candy samples.

Keywords: Multilayer and multichannel membrane filtration; Separation; Enrichment; Diffuse reflectance spectroscopy; Rhodamine B; Acid orange 7.

1. Introduction

Despite the significant advances in analytical instruments in recent years, sample preparations like separation and preconcentration are still the most important and crucial procedures in a whole analytical process. Membrane filtration (Microfiltration) is a pressure driven solid-phase extraction technique with features of rapidity, simplicity of operation, low cost, and high enrichment efficiency. It is often employed to separate and concentrate micron-sized and low concentration particles from fluids with microscopic pores (0.1-10 micrometer) membrane filters. The mechanism of the membrane filtration-enrichment is primarily sieving when the size of particles of the concentrated compound is larger than the pore size of the membrane filter used. If a particle is not much smaller than the pore, then as it passes near the pore there is a definite probability that part of the particle will touch the filter matrix. If adhesive forces are strong enough, the particle will be trapped. In the case of smaller particles, it is presumably attributed to adsorption to the filter surface and in the pore, which is caused by the interactions, including van der Waals forces, electrostatic interaction, hydrophobic interaction, π-π interaction and hydrogen bonding, between the analyte molecule and the filter matrix[1-3]. It has received considerable attention and has been widely used for the separation and preconcentration of trace metallic ions after chromogenic reactions [4-10] and several organic compounds [11-18]. Unlike most of the researches, our group [4, 9, 11, 12] simplified the detection process by omitting the elution step and directly measuring the diffuse reflectance spectrum of the membrane filter concentrated analytes, *i.e.* the on-line spectroscopic determination. It could avoid the use of eluents and also the influence caused by elution operation. More importantly, without eluting process the dilution of the analytes with solvents can be prevented completely, so the enrichment factor is usually very high.

In our previous work [13], a multichannel device was designed for the membrane filtration-enrichment process, which contains six channels and can enrich six samples simultaneously on different positions of a membrane filter. With the assist of the multichannel device, the poor reproducibility of enrichment and on-line detection processes resulted from the differences between membrane filters in traditional method [19-21] had been improved a lot.

However, in case of simultaneously detecting two or more analysts whose absorbance peaks are close or even overlapped in one mixture sample, it is difficult to quantitatively determine the mixtures directly after routine membrane filtration. Sample separation is needed to eliminate the influence arisen from each analyst. In addition, there is another situation that the two or more analysts couldn't all be enriched in one membrane filter, or their most suitable membrane filters are not the same. Thus, effectively simultaneous determination couldn't be fulfilled during one membrane filtration process. In consideration of these circumstances, a very simple but effective mode of multilayer membrane filtration was introduced into the multichannel membrane filtration-enrichment process to achieve the target of separating and enriching analytes simultaneously, and extending the use of membrane filtration-enrichment. The principle of the multilayer membrane filtration mode is filtering the mixture sample solution with two or more different membrane filters which are stacked up at a time. The analytes in mixture solution will be captured by different membrane filters because of the selectivity of membrane filters. Then, spectrum of each analyte can be measured with different membrane filters. In this way, the separation of the mixture is conveniently and easily achieved through one filtration process. Additionally, the application of the proposed method can be extended to real sample analysis, which often has low concentration levels of analytes and high concentrations of interfering matrix components, to reduce or remove compounds initially present in samples that interfere with detection method.

This study was conducted on the basis of our previous research. Two carcinogenic industrial dyes, rodamine B (RhB) and acid orange 7, which are banned as food additives by current legislation in many countries, were used as model analytes to evaluate the effectiveness of the presented method.

2. Experimental

2.1 Chemicals and reagents

All chemicals and reagents used were of analytical purity grade and used without further purification. Rodamine B was purchased from Shanghai Yuanye Biology and Science Co., Ltd, China. Acid orange 7 was purchased from Shanghai Crystal Pure Biological Technology Co., Ltd, China. Mixed cellulose esters (MCA) membrane filter, cellulose acetate (CA) membrane filter, nylon membrane filter, polyethersulfone (PES) membrane filter and polytetrafluoroethylene (PTFE) membrane filter used in the present study were purchased from Xingya (Shanghai Xingya purification materials factory, China) with the pore size of 0.1 um, 50 mm in diameter.

Standard stock solutions of RhB and acid orange 7 with the concentration of 100 μg mL^{-1} were prepared by dissolving the powder reagents with ultra-pure water and stored in a refrigerator. All sample solutions were obtained by stepwise diluting the stock solution with ultra-pure water.

2.2 Apparatus

A miniature fiber optic UV-visible spectrometer USB2000+ (Ocean Optics (Shanghai) Co., Ltd, China) equipped with an integrating sphere accessory was used to collect the UV-Vis spectral data from the membrane filter. A model PHS-25 pH meter (Mettler Toledo instrument (Shanghai) Co., Ltd, China) was used for pH measurement. Ultra–pure water was obtained from an ultra–pure water purification system (SARTORIUS arium 611DI, Germany, 18.2MΩ*cm). Liquid chromatography mass spectrometer (LC-MS, Waters, Xevo G2-S QTof, USA) was utilized to detect the contents of RhB and acid orange 7 for evaluating the enrichment efficiency. SHB–III Vadose water vacuum pump (Shanghai Weikai instrument equipment Co., Ltd, China) was used for the membrane filtration–enrichment.

The membrane filtration–enrichment process was carried out by the homemade six-channel membrane filtration–enrichment device utilized in our previous study [13]. The selected membrane filters were stacked up and placed between the multichannel solution importer and the filtration device (Fig. 1).

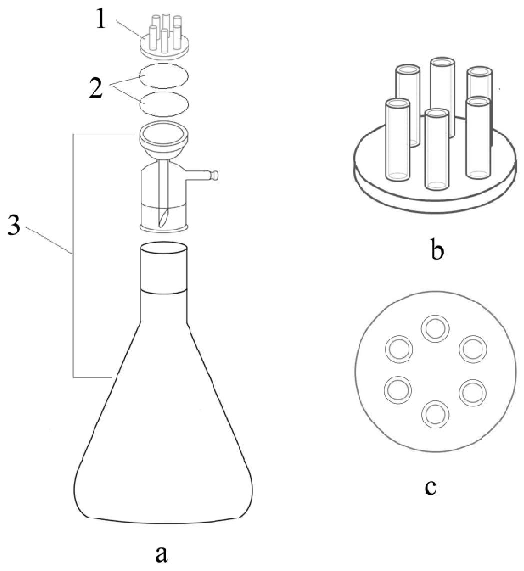

Fig. 1. Schematic of the multichannel membrane filtration–enrichment device (a).1: Acrylic multichannel solution importer; 2: Membrane filters; 3: Filtration device. Schematic of the acrylic multichannel solution importer (b). Top view of the multichannel solution importer (c).

2.3 Experiment procedure

For the multilayer membrane filtration-enrichment procedure under the optimal conditions: a MCA membrane filter was stacked above a nylon membrane filter and they were all placed between the multichannel solution importer and the filtration device, an aliquot of 18 mL sample solution containing RhB and acid orange 7 (without pH adjusting) was loaded into the six-channel membrane filtration-enrichment device and passed through the membrane filters under suction with a vacuum pump at vacuum degree of 0.09 MPa. The analyte RhB was adsorbed by upper MCA membrane filter and acid orange 7 was adsorbed by nylon membrane filter below. After filtration, the membrane filters were air-dried and the UV-Vis diffuse reflectance spectra were on-line measured (without elution) for quantitative analysis, and absorbance peaks at 546 nm and 485nm were considered for RhB and acid orange 7, respectively.

3. Result and discussion

3.1 Selection of membrane filter type

The selection of suitable membrane filters is of great importance to achieve the goal of separating and enriching RhB and acid orange 7. The primary requirement of the membrane filter for the proposed multilayer filtration is enriching analytes selectively. Five commonly used membrane filters, i.e., MCA, CA, nylon, PES, and PTFE membrane filters were tested with RhB and acid orange 7 individual solutions, respectively. The UV-Vis diffuse reflectance spectrum of each membrane filter concentrated RhB or acid orange 7 were measured. According to the results, PTFE membrane filter can barely capture both RhB and acid orange 7, and PES membrane filter shows a faint capacity for enriching the two analytes. Both MCA and CA membrane filters can enrich RhB, and the former provides the strongest absorbance, while they both show negligible capacities for enriching acid orange 7. On the other hand, nylon membrane filter is capable of collecting only acid orange 7. Therefore, in subsequent experiments, MCA and nylon membrane filters were selected as a suitable set for enriching RhB and acid orange 7, respectively.

3.2 Effect of pH

The variation of sample solution pH can lead to the deprotonation or the protonation of a neutral molecule, which will further result in the change of solubility of analytes and the efficiency of the membrane filtration-enrichment procedure. To obtain an appropriate pH for both RhB and acid Orange 7, the effect of each sample solution pH was studied within the range of 1 to 11 adjusted by using HCl and NaOH solutions, respectively. As shown in Fig. 2, under the acid condition, the absorbance of RhB shows a gradually increased tendency, while the suitable pH for Acid Orange 7 is around neutral condition. Taking the sensitivities of detecting both RhB and Acid Orange 7 into account, pH of 4-6 was suitable for this method. The pH of sample solutions were about 5.6. For simplicity, the pH of sample solutions were not adjusted in this work.

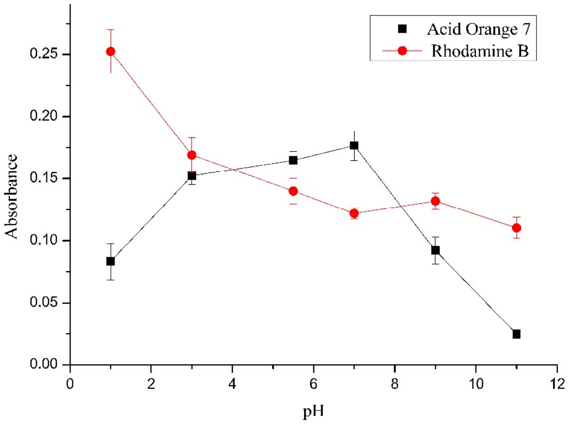

Fig. 2. Effect of pH on absorbance of RhB at 546 nm and acid orange 7 at 485nm. Experiment conditions: concentration of RhB and acid orange 7, 30 μg L^{-1}, vacuum degree, 0.05 MPa; sample volume, 15 mL for RhB and 18 mL for acid orange 7.

3.3 Effect of sample volume

When selecting a suitable sample volume, both the adsorption capacity of the membrane filter and the operation time should be taken into account besides the sensitivity. Mixture sample solutions with different volumes in the range of 5 - 30 mL were filtered under constant conditions. The results listed in Fig. 3 show that as the increase of volume, there is a significant increase on the absorbance of acid orange 7. As for RhB, a growth of the absorbance emerges when the volume rises from 5 to 15 mL, and just a slight variation on the absorbance is observed when the volume is more than 15 mL. Moreover, the operation time for 30 mL was about 10 min which was more than twice that of 15 mL. To reach a compromise, 18 mL of mixture sample solution was adopted in further experiments.

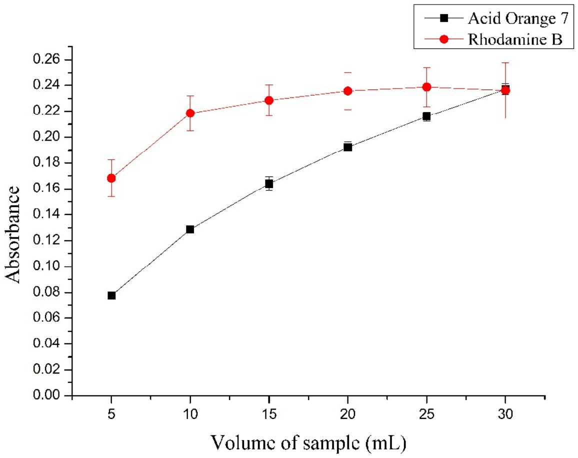

Fig. 3. Effect of sample volume on absorbance of RhB at 546 nm and acid orange 7 at 485nm. Experiment conditions: concentration of RhB and acid orange 7, 30 μg L^{-1}; vacuum degree, 0.095 MPa.

3.4 Effect of vacuum degree

The vacuum degree of a vacuum pump has an immediate impact on the membrane flux and the performance of interactions between analytes and the membrane filter, thus affecting the efficiency of filtration. The effect of vacuum degree was investigated within the range of 0.05 to 0.095 MPa with the mixture sample solution. The results in Fig. 4 illustrate that as the increase of vacuum degree, the absorbance of membrane filters concentrated RhB decrease gradually because of the increase of membrane flux, while that of acid orange 7 increase very slightly. This may be explained by the fact that the low vacuum degree will lead to a low membrane flux and provide enough time for acid orange 7 interacting with upper MCA membrane filter, and this ultimately results in a negligible enrichment of acid orange 7 on MCA membrane filter. When the vacuum degree is 0.09 MPa or above, the time for interaction is not sufficient that acid orange 7 is directly enriched on nylon membrane filter skipping the interaction with MCA membrane filter. Thus the absorbance values of the two analytes remain about the same. Considering both the stability and the operation time, the vacuum degree of 0.09 MPa was selected.

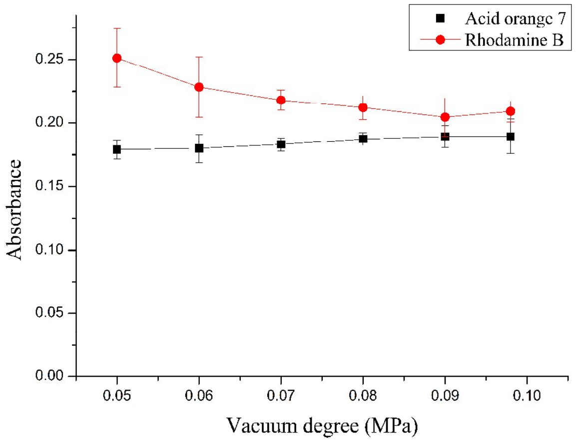

Fig. 4. Effect of vacuum degree on absorbance of RhB at 546 nm and acid orange 7 at 485 nm. Experiment conditions: concentration of RhB and acid orange 7, 30 μg L^{-1}, sample volume, 18 mL

3.5 Separation and enrichment performance of the method

Enrichment efficiency is an intuitional criterion to evaluate the performance of separation and preconcentration of RhB and acid orange 7. The enrichment efficiency of the present method was assessed with 30 μg L^{-1} RhB, acid orange 7 individual solutions and their mixture solution with the help of LC-MS. The analytical results of LC-MS show that the enrichment efficiencies of RhB by upper MCA membrane filter for individual and mixture solutions are 93% and 95%, respectively. And those of acid orange 7 by nylon membrane filter are all above 98%.

The corresponding UV-Vis diffuse reflectance spectra of membrane filters processed with 30 μg L^{-1} RhB, acid orange 7 individual solutions and their mixture solution were measured and illustrated in Fig. 5. According to Fig. 5, the values of absorbance of individual and mixture solutions for RhB are almost the same. As for acid orange 7, the absorbance of mixture solution is just a little higher than that of individual solution. Therefore, it can be regarded that the two analytes don't affect the enrichment of each other.

The UV-Vis spectra of 1000 μg L^{-1} RhB, acid orange 7 and their mixture solutions were directly measured with a 1cm cell and plotted in Fig.6. The UV-Vis diffuse reflectance spectra of membrane filters after the multilayer filtration with 25 μg L^{-1} mixture solution are also plotted. As shown in Fig.6, the absorbance peak of RhB in solution is at 553 nm and that of acid orange 7 is at 485 nm. The two absorbance peaks are very close that the absorbance peak of acid orange 7 in the spectrum of the mixture is covered by that of RhB. Hence, it is difficult to quantitatively analyze acid orange 7 without separation. However, with the help of the multilayer filtration process, individual spectra of the two analytes were obtained from different membrane filters. Because of interaction with the adsorbent, the spactra of analytes adsorbed on the membrane filters is more or less different from those of the free molecules in solutions [22]. On the other side, the values of absorbance of the two analytes adsorbed on the membrane filters all have significant increases compared with those of solutions. These results indicate that after introducing the multilayer membrane filtration mode, the separation and enrichment of the two analytes can easily be implemented.

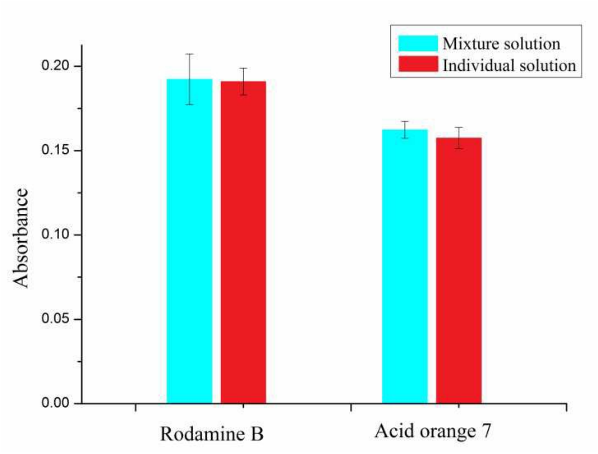

Fig. 5. UV-Vis diffuse reflectance spectra of MCA and Nylon membrane filters after filtering with 30 μg L^{-1} RhB, acid orange 7 individual solutions and their mixture solution (absorbance at 546 nm for RhB and 485 nm for acid orange 7; sample volume, 18 mL; vacuum degree, 0.09 MPa).

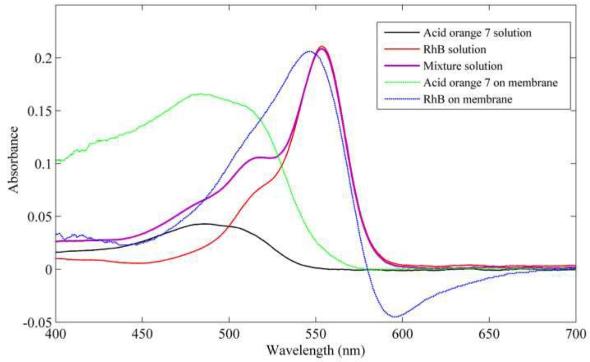

Fig. 6. UV-Vis spectra of 1000 μg L^{-1} RhB, acid orange 7 and their mixture solutions. And UV-Vis diffuse reflectance spectra of MCA and Nylon membrane filters after filtering with 25 μg L^{-1} mixture solutions by the presented multilayer mode (sample volume, 18 mL; vacuum degree, 0.09 MPa).

3.6 Analytical performance of the method

The quantitative relationship between the concentration of RhB in solution and the absorbance of the membrane filter has been investigated in our previous study [13]. Linear models used in this work were also established by the Kubelka-Munk function which reads as follow[23, 24]:

$$F(R_\infty) = (1-10^{-A})^2/2\times10^A = bc$$

Where A is the absorbance of membrane filter concentrated analyte, b is a coefficient and c is the concentration of analyte in the solution.

In the present work, a series of experiments were conducted with RhB and acid orange 7 mixture solutions in the concentration range of 3 – 30 μg L^{-1} and relevant absorbance peaks at 546 nm for RhB and 485 nm for acid orange 7 were measured and plotted in Fig.7. From Fig.7 it follows that linearities of calibration curves for the analytes are achieved only at low concentration levels (here they are 3-9 μg L^{-1} for RhB and 3-20 μg L^{-1} for acid orange 7 with the correlation coefficients (R^2) of 0.9895 and 0.9896), which is consistent with our previous study [13]. The limits of detection, defined as $LOD = 3S_b/m$ (where S_b and m are standard deviation of the blank solution and slope of the calibration curve, respectively), are calculated to be 0.20 μg L^{-1} and 0.24 μg L^{-1}, respectively. Similarly, when c is fitted with A by the Kubelka-Munk function, it provides linear curves with R^2 of 0.9982 for RhB and 0.9952 for acid orange 7. Under the optimal conditions, the repeatability of the proposed method was evaluated using 3, 9 and 20 μg L^{-1} mixture solutions. The relative standard deviations (RSDs) were in acceptable ranges of 3.1%-6.4% for RhB and 2.4%-5.8% for acid orange 7, respectively. The comparisons of the proposed method with other works in some literatures are given in Table 1, which indicates the good performance of the presented method. As mentioned before, the sensitivity of this method is greatly improved, because the on-line determination process excludes the elution operation, which completely prevents the dilution of the analytes with solvents, and retains the high enrichment factor. In addition, the results in Table 1 illustrate that the repeatability of this method is close to other methods and can meet the requirements of trace analysis.

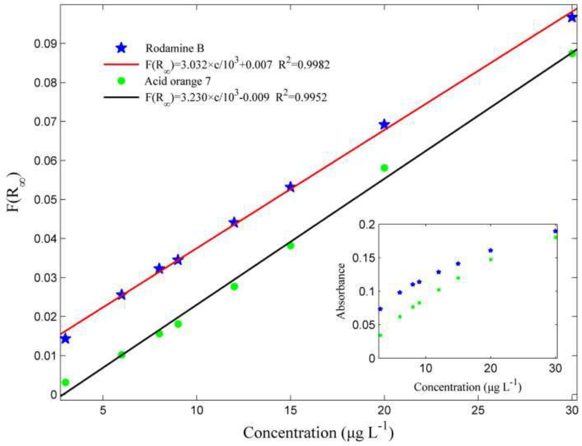

Fig. 7. The relationship of the values of the Kubelka-Munk function $F(R_\infty)$ and RhB and acid orange 7 concentrations in solution in the range of 3-30 μg L^{-1}. The relationship of the absorbance and RhB and acid orange 7 concentrations in solution (inset). Experiment conditions: vacuum degree, 0.09 MPa; sample volume, 18 mL.

Table 1 Performance of some studies on the determination of dyes matter.

Detection system	Analyte	Pretreatment	LOD (μg L^{-1})	RSD (%)	References
UV–visible spectrophotometry	Rhodamine B	Cloud point extraction	1.3	2.40	25
UV–visible spectrophotometry	Rhodamine B	Solid phase extraction (SPE)	3.14	5.0	26
UV–visible spectrophotometry	Rhodamine B	Dispersive liquid–liquid microextraction	6.1	0.9-4.1	27
UV–visible spectrophotometry	Sudan orange G	Membrane filtration	4.9	4.3	28

ion-interaction HPLC	Acid orange 7	Solid phase extraction	7	-	29
UPLC	Acid orange 7	Microwave assisted extraction–SPE	2.16	-	30
UV–visible spectrophotometry	Rhodamine B	Multilayer and multichannel membrane filtration	0.20	3.1-6.4	Present study
	Acid orange 7		0.24	2.4-5.8	

3.7 Real sample analysis

The effect of the potential interfering compounds which usually exist in real samples have been investigated previously. The common inorganic ions won't affect the membrane filtration–enrichment process [13]. In this study, the proposed method was employed to quantify RhB and acid orange 7 in soft drink and candy samples to assess its accuracy and applicability. As a consequence of high contents of carbohydrates in drinks, which are usually macromolecular compounds and will occupy the pore space of the membrane filter, thereby influencing the filtration. The soft drink applied in this study was diluted by 5 times with ultra-pure water. As for candy, besides carbohydrates there are several additives like thickener, emulgator and coating agent, which have strong impacts on the filtration. Thus, candy samples were prepared by dissolving 1 g with 5 mL ultra-pure water and purified by filtering through a PTFE syringe filter for five times and then diluted with ultra-pure water to 100 mL. No RhB and no acid orange 7 was detected in the two real samples even though sample solutions with large volumes were processed, so the soft drink and candy samples were spiked with RhB and acid orange 7 at the concentrations of 5, 10 and 15 μg L^{-1}, respectively, to prepare man-made samples. Recovery experiments were conducted and the results are listed in Table 2. The recoveries of the target analytes are in acceptable ranges of 92.8-109.7% for RhB and 90.5-111.5% for acid orange 7 with all RSDs (n=3) less than 9.2%, which verifies the feasibility of the current method.

Table 2 Application of the proposed method for determination of rhodamine B and acid orange 7 in different real samples. Experiment conditions: vacuum degree, 0.09 MPa; sample volume, 18 mL.

Sample	Analytes added	Rhodamine B found	Recovery[a] (%)	RSD (%)	Acid orange 7 found	Recovery[a] (%)	RSD (%)
Soft drink (μg L^{-1})							
	-	ND	-	-	ND	-	-
	25	23.2	92.8	7.2	24.9	99.8	2.2
	50	54.8	109.7	9.2	53.2	106.4	1.8
	75	76.9	102.6	5.9	83.6	111.5	3.3
Candy (μg g^{-1})							
	-	ND	-	-	ND	-	-
	0.5	0.52	105.5	7.8	0.51	101.5	4.3
	1.0	1.04	105.7	8.2	0.91	90.5	1.2
	1.5	1.48	98.2	1.6	1.45	96.9	3.1

[a] Average of three independent measurements

4. Conclusions

In summary, we have initially presented a novel mode of multilayer membrane filtration which can provide a simple way to simultaneously separate and concentrate analytes in mixture samples, and extend the application of membrane filtration-enrichment. The proposed approach was evaluated by detecting rhodamine B and acid orange 7 in their mixture samples as a case study. The main parameters influencing the multilayer and multichannel filtration process were thoroughly optimized. The results reveal that the developed multilayer mode is facile and efficient. With its help, analytes in the mixture solution are separated and collected by different membrane filters because of the selectivity of membrane filters. Thus, individual spectrum of each analyte is easily obtained from different membrane filters. Good sensitivity and repeatability of the multichannel membrane filtration–enrichment technique which have been proved in our previous study were also obtained in this method. Moreover, the applicability of it can also be extended to real sample analysis to reduce or remove the interference of matrix or other compounds initially present in samples.

Acknowledgement

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References

1. Sheng Chang, T David Waite, Andrea I Schäfer and A. G. Fane, *Environ. Sci. Technol.*, 2003, **37**, 3158-3163.
2. A. I. Schafer, I. Akanyeti and A. J. Semiao, *Adv. Colloid Interface Sci.*, 2011, **164**, 100-117.
3. T. D. Brock, *Science Tech*, 1983.
4. J. Iqbal, C. Yin, J. Geng, X. Li, X. Li, Y. Du and B. X. Liu, *Microchimica Acta*, 2012, **177**, 195-200.
5. I. Narin and M. Soylak, *Anal. Chim. Acta*, 2003, **493**, 205-212.
6. I. M. Raimundo and R. Narayanaswamy, *Sensor actuat B-Chem*, 2003, **90**, 189-197.
7. Y. Takahashi, H. Kasai, H. Nakanishi and T. M. Suzuki, *Angew Chem Int Ed Engl*, 2006, **45**, 913-916.
8. U. Divrikli, A. A. Kartal, M. Soylak and L. Elci, *J. Hazard. Mater.*, 2007, **145**, 459-464.
9. C. H. Yin, J. Iqbal, H. L. Hu, B. X. Liu, L. Zhang, B. L. Zhu and Y. P. Du, *J. Hazard. Mater.*, 2012, **233**, 207-212.
10. Z. A. Alothman, Y. E. Unsal, M. Habila, M. Tuzen and M. Soylak, *Desalination and Water Treatment*, 2015, **53**, 3457-3465.
11. X. H. Yang, B. X. Liu, T. Wu and Y. P. Du, *Analytical Letters*, 2013, **46**, 2410-2420.
12. G. Chen, H. Hu, T. Wu, P. Tong, B. Liu, B. Zhu and Y. Du, *Food Control*, 2014, **35**, 218-222.
13. W. Li, L. Wang, P. J. Tong, J. Iqbal, X. F. Zhang, X. Wang and Y. P. Du, *RSC Adv.*, 2014, **4**, 52123-52129.
14. V. Vasquez, M. E. Baez, M. Bravo and E. Fuentes, *Analytical and bioanalytical chemistry*, 2013, **405**, 7497-7507.
15. A. Canas, P. Richter and G. M. Escandar, *Anal Chim Acta*, 2014, **852**, 105-111.
16. Z. A. AlOthman, Y. E. Unsal, M. Habila, A. Shabaka, M. Tuzen and M. Soylak, *Food Chem. Toxicol.*, 2012, **50**, 2709-2713.

17. K. Chajara, C. H. Andersson, J. Lu, E. Widenkvist and H. Grennberg, *New J. Chem.*, 2010, **34**, 2275-2280.
18. Z. Y. Yeo, S. P. Chai, P. W. Zhu, S. K. Mah and A. R. Mohamed, *New J. Chem.*, 2015, **39**, 4135-4140.
19. J. S. Fritz, M. P. Arena, S. A. Steiner and M. D. Porter, *J. Chromatogr. A*, 2003, **997**, 41-50.
20. M. P. Arena, M. D. Porter and J. S. Fritz, *Anal. Chim. Acta*, 2003, **482**, 197-207.
21. M. P. Arena, M. D. Porter and J. S. Fritz, *Anal. Chem.*, 2002, **74**, 185-190.
22. G. KORTUM and W. BRAUN, *Angew Chem Int Ed*, 1963, **2**, 333-341.
23. P. Kubelka and F. Munk, *Zeitschrift fur Technische Physik*, 1931, **12**, pp. 596-601.
24. P. D. G. Kortüm, *Springer Berlin Heidelberg*, 1969, pp. 5-216.
25. N. Pourreza, S. Rastegarzadeh and A. Larki, *Talanta*, 2008, **77**, 733-736.
26. M. Soylak, Y. E. Unsal, E. Yilmaz and M. Tuzen, *Food Chem. Toxicol.*, 2011, **49**, 1796-1799.
27. W. Li, X. Zhang, P. Tong, T. Wu, H. Hu, M. Wang and Y. Du, *Spectroc. Acta Pt. A- Mol Biomol Spectrosc*, 2014, **124**, 159-164.
28. A. L. ZA, Y. E. Unsal, M. Habila, A. Shabaka, M. Tuzen and M. Soylak, *Food Chem. Toxicol.*, 2012, **50**, 2709-2713.
29. M. Perez-Urquiza, M. D. Prat and J. L. Beltran, *J. Chromatogr. A*, 2000, **871**, 227-234.
30. H. Sun, N. Sun, H. Li, J. Zhang and Y. Yang, *Food Analytical Methods*, 2013, **6**, 1291-1299.

Figure caption:

Fig. 1. Schematic of the multichannel membrane filtration–enrichment device (a).1: Acrylic multichannel solution importer; 2: Membrane filters; 3: Filtration device. Schematic of the acrylic multichannel solution importer (b). Top view of the multichannel solution importer (c).

Fig. 2. Effect of pH on absorbance of RhB at 546 nm and acid orange 7 at 485nm. Experiment conditions: concentration of RhB and acid orange 7, 30 μg L^{-1}, vacuum degree, 0.05 MPa; sample volume, 15 mL for RhB and 18 mL for acid orange 7.

Fig. 3. Effect of sample volume on absorbance of RhB at 546 nm and acid orange 7 at 485nm. Experiment conditions: concentration of RhB and acid orange 7, 30 μg L^{-1}; vacuum degree, 0.095 MPa.

Fig. 4. Effect of vacuum degree on absorbance of RhB at 546 nm and acid orange 7 at 485 nm. Experiment conditions: concentration of RhB and acid orange 7, 30 μg L^{-1}, sample volume, 18 mL

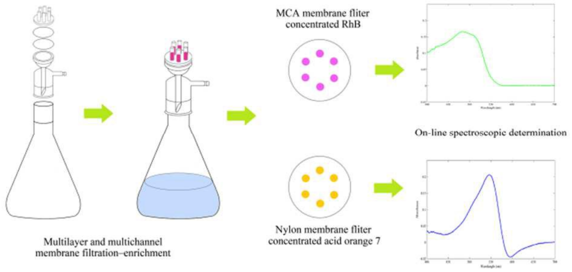
Fig. 5. UV-Vis diffuse reflectance spectra of MCA and Nylon membrane filters after filtering with 30 μg L^{-1} RhB, acid orange 7 individual solutions and their mixture solution (absorbance at 546 nm for RhB and 485 nm for acid orange 7; sample volume, 18 mL; vacuum degree, 0.09 MPa).

Fig. 6. UV-Vis spectra of 1000 μg L^{-1} RhB, acid orange 7 and their mixture solutions.

And UV-Vis diffuse reflectance spectra of MCA and Nylon membrane filters after filtering with 25 μg L^{-1} mixture solutions by the presented multilayer mode (sample volume, 18 mL; vacuum degree, 0.09 MPa).

Fig. 7. The relationship of the values of the Kubelka-Munk function $F(R_\infty)$ and RhB and acid orange 7 concentrations in solution in the range of 3-30 μg L^{-1}. The relationship of the absorbance and RhB and acid orange 7 concentrations in solution (inset). Experiment conditions: vacuum degree, 0.09 MPa; sample volume, 18 mL.

Graphical Abstract



A multilayer and multichannel membrane filtration–enrichment method was developed to simultaneously separate and enrich trace analytes in mixture samples.