嘉南藥理科技大學專題研究計畫成果報告

面皰製品中硫成分測定方法之研究

計畫類別：個別型計畫
計畫編號：CNAC-93-03
執行期間：93 年 1 月 1 日至 93 年 12 月 31 日

計畫主持人：王來好　教授

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一、中文摘要

本研究利用簡單且快速的硫離子選擇電極，測定化妝品中硫成分。線性範圍１～300 mg L^{-1}，偵測極限 0.04 mg L^{-1}。測定結果與高效能液相層析法有 98%一致。

關鍵詞：
硫，　離子選擇電極,
化妝品與藥品的產品

Abstract

A simple and rapid method to determine sulfur in cosmetic products was described using sulfide ion-selective electrode. The linearity of the calibration curve is relatively large, generally covering a 1 to 300 mg L^{-1} range and detection limit is 0.04 mg L^{1}. Comparision with results obtained from high-performance liquid chromatography shows 98 % good agreement.

Keywords: Sulfur, ion-selective electrode, cosmetic products..

二、緣由與目的

Sulfur is often prescribed as an anti-inflammatory, an antiseptic, or a kerotolytic of topical pharmaceutical or cosmetic preparations for treatment of skin disorders. The Taiwan cosmetic law No.44611, the limit usage of precipitated sulfur as anti-acne agents in acne cream is allowed at level of 2 % (m/m). Its evaluation and analytical control in drugs and cosmetics require methods capable of distinguishing the type of sulfur present either as an active ingredient or as a constituent in raw materials used for cosmetics formulation. Many analytical methods have been described for the determination of sulfur. These paper included x-ray fluorescence [1], inductively coupled plasma (ICP) technique [2-4], voltammetry [5-9], ion chromatography [10-13], gas chromatogra phy [14], high-performance liquid chromatography [15-17]. ICP techniques offer the possibility of rapid and simultaneous multi-element determinations, but the instruments for this purpose are very expensive.

Sulfur-containing compounds can be measured by gas chromatography on a packed non-polar column with flame photometric detection. The elemental sulfur does not appear in a chromatographically homogeneous form. Several peaks were observed that could be ascribed to the molecular forms S_2-S_8. However, there are very few reports in literature concerning the determination of sulfur in cosmetic creams and pharmaceuticals. At present, there are several methods of indirect determination, involving tedious and time-consuming sample preparation, the sulfur is oxidized to sulfate ion and monitored by ion chromatography, titration, and precipitation. Ion-selective electrode assures the reliability of analytical information in cosmetic and pharmaceutical products assay due to the possibility to determine directly, without any prior separation, the activity of ions in solution. Therefore, efforts were made to find a relatively simple and fast method for sulfur determination, which would not require expensive instruments. Elemental sulfur dissolves in alkaline solution of sulfides. Indirect voltammetric determinations based on the transformation of the analyzed substances into a sulfide, which is a convenient method for determining sulfur element. In this study, a solution of hydrazine hydrate was used as the alkaline medium. The optimal conditions for sulfur determination by ion-selective electrode and high performance liquid chromatography.

實驗條件

Apparatus

All absorbance measurements were using a Shimadzu model 1201 spectrophotometer at 262 nm. HPLC was performed with an Hitachi model L-7100 pump and model 7125 injector equipped with 20 μL sample loop and a Shimadzu SPD 10A multi wavelength spectrophotometric detector. The soluble sulfide concentration was determined with a silver/sulfide combination electrode (Phonix electrode company istek, INC) and an Orion model 420 mV Meter.

Reagents

Precipitated sulfur was obtained from Strem. Other chemicals were of reagent grade. Cosmetic products containing sulfur were obtained from commercial sources.

Procedures

Sulfide anti-oxidant buffer (SAOB), this buffer must be used fresh and will range in color from clear to yellow-brown .It has become oxidized when it turns dark brown and should then be discarded. The absorbing solution (SAOB) for sulfide was prepared with 50ml of 1N NaOH, 2 grams of ascorbic acid, and 0.5 grams of disodium EDTA, swirl the mixture until the solids dissolve and fill to a 250ml volumetric flask and mark with distilled, deaerated water. Stock solution of sulfur was prepared by dissolving the appropriate of sulfur in cyclohexane and hydrazine hydroxide, respectively. A set of standard solutions were produced by diluting aliquots of the stock solutions with cyclohexane and SAOB buffer to 10 mL in volumetric flasks, respectively.

Taking into about the content of sulfur in anti-acne cream, and whitening cream, a sample (approx. 0.05~0.5g) of the latter were weighed accurately in 50 mL beaker, diluted with about 20 mL cyclohexane and hydrazium hydroxide dissolved and filtered into a 25 mL volumetric flask and make up to volume with cyclohexane and SAOB, respectively.

三、結果與討論

Calibration graph

To make a calibration graph of sulfide, a series of sulfide solutions taken in volumetric flasks were diluted to 25 mL with the SAOB buffer. The electrode potential of each solution was measured as in the above procedure. The resulting plot at 25℃ was shown in Fig. 1 for sulfide. Linear relationship was obtained in the range from 1 to 300 mg L^{-1} for sulfide. This range of concentration can be estimated enough to cover the contents of sulfur in cosmetic products.

SAOB (absorbing solution)

The mixture solution of sodium hydroxide, ascorbic acid and EDTA is very effective for sulfide to keep stable. The sulfide ion in this solution was successfully determined by sulfide ion-selective electrode.

Precision of analysis

To evaluate the precision of analysis by this method, recovery testes were carried out on cosmetic products. Two cosmetic products were spiked with the amounts Reported in Table 1 and subjected to the whole procedure. As shown in Table 1,excellent recoveries and precision were observed (97%).

Application to cosmetic products

The proposed ion-selective electrode method was applied to the determination of kera tolytic agent in cosmetic products (acne creams and whitening creams).

Fig. 2 shows absorption spectrum of commercial lotion. The Table 2 lists the results from the determination of sulfur five commercial cosmetic products. These results agreed with those obtained by a HPLC method, which was carried out with Hypersil ODS column (25 cm x 4.6 mm, i. d) with ultraviolet two channels at 262 and 320 nm detection.

Conclusions

The Sulfide ion-selective electrode procedures described here are applied directly to the analysis of cosmetic samples without the need for precipitated sulfur prior separation. The direct determination of sulfide not only offers more precise than indirect determination but also saves more time. The linearity of the calibration curve is relatively large, generally covering a1 to 300 mg L^{-1} range and detection limit is 0.04 mg L^{-1}.The time and cost of one determination with ion-selective electrode are substantially reduced.

Acknowledgement

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Table 1 Recovery and reproducibility in the analysis of ance-cream and whitening cream by sulfur-ion selective electrode.

	Added (mg L^{-1})	Found (mg L^{-1})	Recovery [a] (%)
Acne cream	5.00	4.84	97(3.8%) [b]
Whitening cream	2.00	1.94	97(4.9%)

[a] Number of determination [N=6]

[b] Relative Standard deviation

Table 2 Analytical results for the determination of sulfur in commercial acne-cream and whitening cream by HPLC and sulfur ion selective electrode.

Cosmetics	Concentration(%,w/w)[a]	
	LC-UV	sulfur-ion electrode
Acne cream 1	7.51(0.1%)[b]	7.28(3.0%)
Acne cream 2	3.426(1.3%)	3.268(2.3%)
Acne cream 3	1.245(1.1%)	1.286(2.1%)
Whitening cream 1	0.527(0.2%)	0.555(1.2%)
Whitening cream 2	0.221(1.7%)	0.218(2.1%)

[a] Number of determination [N=6]

[b] Relative Standard deviation

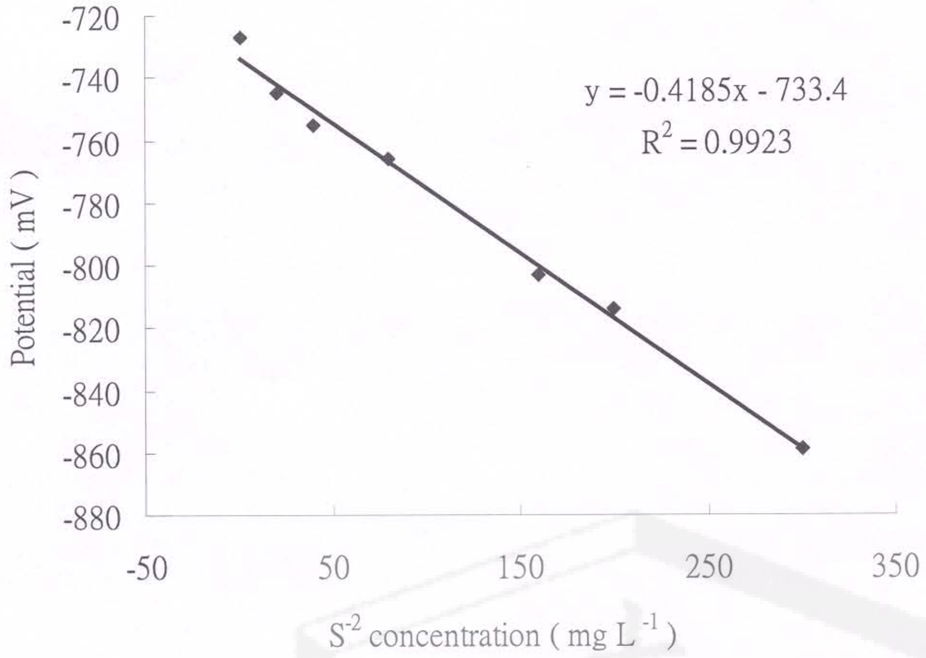

Figure 1 Calibration curve and correlation from sulfide.

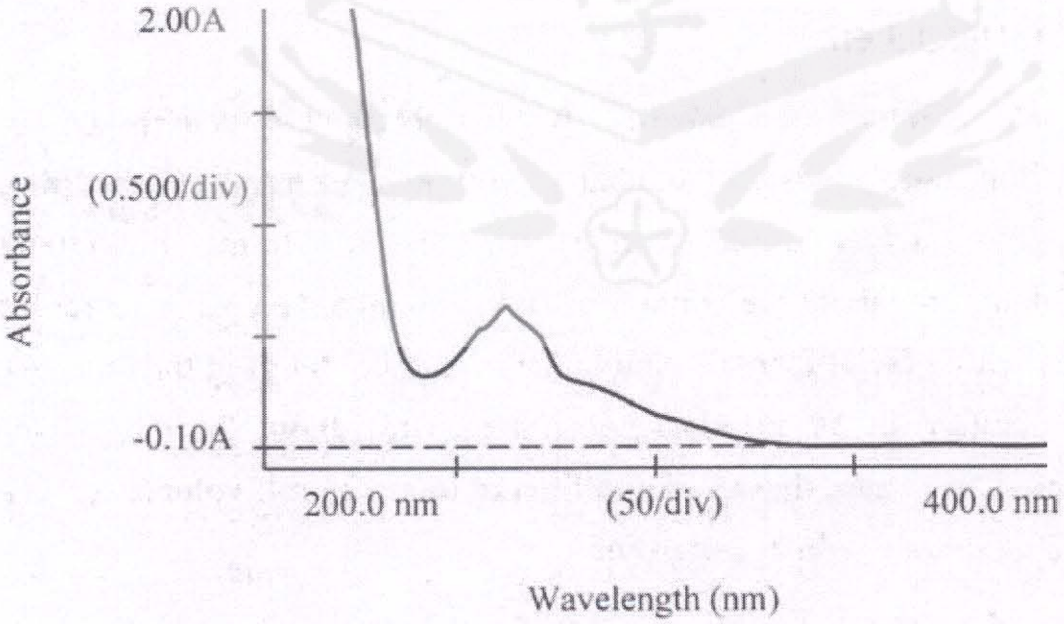

Fig. 2 Absorption spectrum of commercial lotion in cyclohexane. Conditions: cell lengh, 1 cm.