Determination of Sulfur Dioxide in Starch and Other Pharmaceutical Materials

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Abstract □ A sensitive and selective polarographic method for the measurement of sulfur dioxide in a wide variety of pharmaceutical materials is presented. It is based on the combination of its reducibility and volatility.

Keyphrases □ Starch—polarographic determination of sulfur dioxide content □ Sulfur dioxide—polarographic determination in starch and pharmaceutical materials □ Polarography—analysis, sulfur dioxide in starch and pharmaceutical materials

The polarographic reduction of sulfur dioxide in acid medium first was described by Gosman (1) and subsequently was elucidated by Kolthoff and Miller (2). The volatility of sulfur dioxide may be used to avoid a classical limitation of trace analysis: uncertainties in the blank and matrix corrections. This is accomplished by making the polarographic measurement, flushing sulfur dioxide from the system with an inert gas stream, and then remeasuring to obtain the residual current due to the sample, supporting electrolyte, impurities, *etc.*

EXPERIMENTAL

A suspension of starch (200 mg/10 ml of deoxygenated pH 8.3 Britton–Robinson buffer) was stirred while deoxygenating for 5 min in a polarographic cell thermostatted at 10°. After diverting the nitrogen flow over the surface of the solution, 1.0 ml of deoxygenated 3 *M* HCl was added, the suspension was stirred for 30 sec, and the current was measured. Nitrogen then was passed through the suspension to eliminate the sulfur dioxide and the residual current was measured. Finally, 50 μl of standard sulfite solution (5 mg $Na_2S_2O_5$/10 ml deoxygenated pH 8.3 buffer), corresponding to 80 ppm of sulfur dioxide in the sample, was added and the current was measured after stirring briefly. The current obtained after the standard addition of 80 ppm, the USP limit for sulfur dioxide in starch, was compared with that obtained for the sample originally. Alternatively, a calibration curve covering the concentration range of interest was prepared and the actual value was determined.

RESULTS AND DISCUSSION

In the case of capsule food starch samples, differential pulse polarography[1] gave a clearly defined and well-separated reduction peak at −0.35 v *versus* silver–silver chloride (saturated potassium chloride) electrode; the peak current was linear with sulfur dioxide concentration over the range studied: 5–200 ppm in the sample. Since none of the samples examined contained significant amounts of sulfur dioxide, both the precision and accuracy of the polarographic determination were evaluated on capsule food starch "spiked" with sulfur dioxide by equilibrating the sample with the gas in a closed vessel. The precision of the method (*ts*) was ±19% at the 95% confidence level for 6 degrees of freedom. In view of this precision, the polarographic average (223 ppm sulfur dioxide) is in good agreement with the value (244 ppm sulfur dioxide) obtained by the USP (3) iodometric titration method.

In the presence of starch, responses obtained upon standard additions of sulfur dioxide were 20% lower than in the absence of starch; calibration curves must be prepared using a sample suspension to account for such matrix effects. If no sulfur dioxide reduction wave is evident and if subsequent standard additions provide increases in current that are less than proportional to the amount added, the presence of oxidizing substances is indicated. With a few pregelatinized starch samples, a wave preceding that of sulfur dioxide also diminishes upon flushing with nitrogen, changing the residual current in the region of the wave; when this is compensated for, excellent recoveries are obtained upon addition of known quantities of sulfite.

In addition to starch, the method has been applied (using conventional dc polarographic equipment[2] or rapidly dropping mercury electrodes) to the determination of sulfite in the presence of menadiol sodium diphosphate, levodopa, canthaxanthin, iproniazid (4), trimethoprim, sulfisoxazole, sulfamethoxazole, influent and effluent water streams, and sulfuryl chloride. Only in the last case was it necessary to modify the procedure by using excess sodium hydroxide to neutralize acids generated as the sample dissolved. In all cases the sample should be acidified just prior to polarography and stirring should be kept to a minimum or the volatility of sulfur dioxide will lead to erratic results even at 10°.

Under the recommended conditions, the response is not significantly changed after 5 min; it decreases only 8% after 20 min with the starch samples, for example.

The recommended method does not require distillation, filtration, or other manipulation resulting in loss of sulfur dioxide. In addition to its relative simplicity, the method requires a minimal quantity of sample due to its high sensitivity, is virtually specific for sulfur dioxide, and is applicable to a wide variety of materials.

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[1] Princeton Applied Research model 174 polarographic analyzer.

[2] Metrohm Polarecord E261-R.