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THE ANALYSIS OF TBP PROCESS STREAMS FOR CALCIUM WITH THE FLAME PHOTOMETER

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Introduction

An accurate determination of small amounts of calcium present in the RAF, RAS, RAW, and RCX streams of the TBP Process was desired. Flame photometric analysis was selected as the method affording the most sensitivity for the determination. It was apparent that some interference would occur due to the high salt content of the RAF and RAW streams, and initial experiments were directed toward obtaining an understanding of these interferences. A Beckman spectrophotometer, Model DU, equipped with a Beckman #9200 flame photometry attachment and a photomultiplier attachment was used for all flame emission measurements.

Summary

A method was found for determining calcium concentrations in TBP process streams in spite of serious interferences by sodium, ferrous, uranyl, sulfate, phosphate, and sulfamate ions as well as by TBP. The precision attainable varied from sample to sample, depending upon its composition. In general, errors of 20% or greater occurred. The smallest determinable amount of calcium was about 10 mg/l.

Preliminary Experiments

The sodium content of the RAF and RAW streams is 64 and 49 g/l, respectively. Since the probable amount of calcium present is about 20 mg/l, an extremely large Na/Ca ratio exists. The effect of sodium on the flame emission of calcium was therefore investigated. Three separate mechanisms of interference by sodium were

found to occur, the most serious of which was the continuous flame spectrum of sodium. Second in importance was the enhancement of calcium emission by sodium. Finally, some stray light of 589 mu wavelength from the intense emission line of sodium was shown to be passing the monochromator and reaching the phototube.

It was found that all three of the above interferences could be corrected for by using calcium as its own internal standard. Increasing amounts of calcium were added to aliquots of a solution containing known amounts of sodium and calcium. The flame emission of calcium was then measured at the 422.4 mu emission line and corrected for sodium background by measuring at a point a few millimicrons away. The net calcium emission was plotted against the amount of calcium added. By extrapolating the curve to zero emission, the calcium concentration of the unspiked aliquot was obtained. An advantage of the method is that all suppression and enhancement interferences are corrected for inherently. It is thus possible to apply the method to the analysis of complex mixtures without determining the effect of each component on the emission by calcium.

To test the method, a solution approximating the composition of the RAW was prepared, and known amounts of calcium were added to aliquots. The aliquots were analyzed for calcium by the foregoing method. An unspiked aliquot was also analyzed to correct for the calcium present in the reagents. A final dilution factor of 1:200 was necessary to eliminate plugging of the aspirator due to deposition of solid sodium salts on the burner tip. Results are shown in the following table.

TABLE I

ANALYSIS OF SYNTHETIC RAW SOLUTION

Ca Present, mg/l	Ca Added to 1:200 dilution, mg/l	Emission 422.4 mu-418 mu	Ca Found, mg/l	Ca Found, mg/l (Corrected for blank)
200	0	9.8	228	222
"	0.5	13.6		
"	1.0	16.4		
"	1.5	19.9		
100	0	6.2	136	130
"	0.5	9.9		
"	1.0	13.6		
"	1.5	16.6		
50	0	3.9	60	54
"	0.25	7.0		
"	0.50	8.9		
"	0.75	11.0		
25	0	2.4	28	22
"	0.25	5.0		
"	0.50	8.6		
"	0.75	10.7		
0	0	0.6	6	0
"	0.25	4.4		
"	0.50	6.5		
"	0.75	9.4		

As may be seen from the preceding data, the uncertainty in extrapolating a relatively large portion of the curve is great, and for this reason, it is better to work with a dilution containing only a small amount of calcium in excess of the detection limit. A minimum of 0.05 mg/l Ca may be determined in this manner, which corresponds to 10 mg/l Ca in the solution before dilution. The error in extrapolating the curve is caused by its non-linearity, and an average error of about 20% occurs.

Analysis of Plant Samples

A series of TBP process samples, which consisted of the RAF, RAS, and RAW streams, was analyzed for calcium by the method described here. In addition, the RCX stream, which is 0.01 M HNO_3 only, was analyzed by conventional flame photometric methods and found to contain less than 0.1 mg/l Ca.

The emission measurements of the 1:200 dilutions of the RAF, RAS, and RAW streams are shown in the following table.

TABLE II

ANALYSIS OF TBP PROCESS SAMPLES

Stream	mg/l Ca Added	Emission 422.4 mu-418 mu
RAF	0.4	4.4
"	0.3	3.9
"	0.2	3.1
"	0.1	2.2
"	0	1.1
RAS	0.4	7.2
"	0.3	5.7
"	0.2	4.0
"	0.1	2.6
"	0	1.1
RAW	0.4	4.2
"	0.3	3.9
"	0.2	3.3
"	0.1	2.6
"	0	1.6

Plotting the measured emissions against the concentrations of added calcium resulted in smooth curves which could be readily extrapolated to zero emission. The calcium concentration of the aliquot containing no added calcium was obtained from the extrapolated curve. The corresponding calcium concentrations of the samples were found to be as follows:

Stream	Ca Found, mg/l
RAF	18
RAS	12
RAW	20

It should be noted that a rubber stopper had been used to seal the initial RAW sample. It has been observed by the writer that black rubber materials, such as stoppers, medicine dropper bulbs, and wash bottle bulbs, are leached by aqueous solutions, introducing significant amounts of calcium to the solution. For this reason, the value reported for the RAW is probably high.

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