Table II (*Continued*)

Erythromycin *N*-oxide			*O*,*N*-Dicarbethoxy des-*N*-methylerythromycin			Erythralosamine			Desosamine Hydrochloride	
d, A.	I/I_1	*hkl*	*d*, A.	I/I_1	*hkl*	*d*, A.	I/I_1	*hkl*	*d*, A.	I/I_1
11.04	0.50	011	15.36	0.53	110	13.61	0.13	100	8.30	0.50
10.15	1.00	101	11.18	0.67	020	10.77	0.53	$00\underline{1}$	7.36	0.38
9.01	0.30	111	9.67	1.00	011	8.49	0.33	$10\bar{1}$	6.05	0.50
8.44	0.20	120	8.83	0.67	111	7.61	0.27	$01\underline{1}$	5.87	0.13
8.00	0.20	200	7.50	0.33	201	6.56	1.00	$11\bar{1}$	5.63	0.13
7.40	0.10	210	7.10	0.33	211	5.67	0.13	201	4.84	0.13
7.03	0.10	121	6.08	0.13	230	5.37	0.27	002, $\underline{0}20$	4.39	1.00
6.51	0.30	002	5.85	0.07	320	4.99	0.53	$10\bar{2}$	4.24	0.38
6.21	0.50	220, 012	5.67	0.13	040	4.81	0.13	$02\underline{1}$	4.10	0.25
5.80	0.10	112	5.25	0.27	012	4.49	0.20	$12\bar{1}$	3.76	0.25
5.52	0.20	131	5.09	0.13	112	3.91	0.07	...	3.64	0.06
5.08	0.20	310	4.80	0.07	022	3.82	0.03	...	3.51	0.25
4.78	0.20	311	4.72	0.13	420	3.32	0.07	...	3.42	0.63
4.61	0.20	032	4.62	0.07	212	3.27	0.07	...	3.10	0.13
4.44	0.20	132	4.47	0.13	251				2.83	0.13
4.27	0.05	013, 240	4.27	0.07	430				2.77	0.06
4.17	0.05	330	4.10	0.07	510				2.62	0.06
4.00	0.20	400	4.00	0.13	232				2.58	0.06
3.83	0.10	401, 123, 142	3.71	0.07	060					
3.71	0.10	420	3.54	0.07	422					
3.51	0.05	242	3.25	0.07	360					
3.38	0.05	303								
3.32	0.10	...								
2.89	0.05	...								
2.81	0.05	...								

SCIENTIFIC COMMUNICATION

Ethylmethylpicrate as a Reagent for Barium

IN AN exploratory investigation of the properties of certain trinitrophenols as analytical reagents, we have observed that 3-ethyl-5-methyl-2,4,6-trinitrophenol (hereafter called ethylmethylpicric acid for short) has considerable promise as a precipitation reagent for barium. For its practical application as a reagent, a saturated aqueous solution of its sodium salt appears to be more useful than the acid itself, and a preliminary study of the value of the reagent in this form is here reported.

Neither this acid nor any of its salts appears to have been previously reported. The following simple method for synthesizing ethylmethylpicric acid was found to be satisfactory.

Add 10 grams of 1,3,5-ethylmethylphenol (Eastman Kodak Co.) to 50 grams of 95% sulfuric acid and heat to 60° C. Cool to about 5° C. and add 70% nitric acid with constant stirring at such a rate that the temperature does not rise above 15° C. Dropwise addition is advisable at the beginning. Continue adding the nitric acid until a total of 35 grams has been added. Allow to stand overnight and then pour the reaction mixture on an equal volume of cracked ice. Filter off the insoluble material, preferably on a suction filter, and dissolve it in warm 95% ethyl alcohol. Add 10% potassium hydroxide to the solution until no more precipitate forms. Filter off the potassium salt and dissolve it in hot water. Add 38% hydrochloric acid dropwise with constant stirring until no more precipitate forms. Filter off the precipitate, dissolve it in 95% ethyl alcohol for recrystallization, and dry the final product at room temperature. The yield should be about 90%.

For the preparation of 100 ml. of a saturated solution of the sodium salt, place 3 grams of the dried acid in 75 ml. of water and slowly add 10% sodium hydroxide until the pH of the mixture as measured with the glass electrode becomes 7. Dilute to 100 ml. and use the clear supernatant liquid.

Analyses of the barium salt precipitated in water solution at room temperature and dried at various temperatures up to 100° C. showed that it has the formula $Ba(C_9H_8N_3O_7)_2.H_2O$. Its theoretical barium content is 19.70%. This salt loses its water of hydration at higher temperatures, and at 150° C. the rate of loss is easily observable. The dehydration is accompanied by a marked change of color from yellow to dark orange.

In spite of the appreciable solubility of this barium salt in water (0.12 gram per 100 ml. at 25° C.), its precipitation is practically quantitative if a sufficient excess of reagent is used. Satisfactory results have been obtained gravimetrically for barium alone, for barium in the presence of an equal amount of calcium by single precipitation, and for barium in the presence of an equal amount of strontium or potassium by double precipitation.

This reagent seems especially convenient for the rapid spectrophotometric determination of amounts of barium up to about 15 mg. The following procedure has been developed and tested.

Adjust the concentration of the neutral barium solution contained in a 100-ml. beaker to about 2 mg. per ml. Add 15 ml. of reagent and allow the mixture to stand at room temperature for half an hour. Remove the supernatant liquid with a filter stick and wash with successive small portions of ethyl ether, or with ethyl ether saturated with barium ethylmethylpicrate, until the washings become colorless. Dissolve the precipitate in about 50 ml. of warm water, cool the solution, and transfer it to a 100-ml. volumetric flask with the aid of successive small portions of water. Dilute to the mark, mix, and use the solution directly for measurement when the amount of barium is small, or for further dilution when the amount of barium is high.

Results of test determinations by the above procedure are shown in Table I. The instrument used was a Beckman spectrophotometer, Model DU, with a 1.00-cm. cell. The measurements were made at 390 mμ. That there is a well defined maximum at about this point is shown by the data in Table II. These measurements were made on a barium ethylmethylpicrate solution having a concentration of 4.98 mg. per 100 ml. contained in a 1.00-cm. cell. The relationship between light absorption and concentration was found to be closely proportional for solutions of this salt.

Table I. Spectrophotometric Estimation of Small Amounts of Barium

No.	Degree of Dilution of Original Solution of Precipitate	Absorbancy	Barium Taken, Mg.	Barium Found, Mg.	Difference Error, Mg.
1	None	0.206	0.3	0.3	0.0
2	None	0.620	1.0	0.9	−0.1
3	None	0.650	1.0	1.0	0.0
4	2.5 times	0.510	2.0	1.9	−0.1
5	2.5 times	0.830	3.0	3.1	+0.1
6	2.5 times	0.820	3.0	3.1	+0.1
7	5 times	0.670	5.0	5.0	0.0
8	10 times	0.900	13.9	13.6	−0.3

Table II. Light Absorption of Barium Ethylmethylpicrate Solution

Wave Length, mμ	Absorbancy
350	0.455
360	0.535
370	0.611
380	0.634
390	0.660
400	0.600
410	0.511
420	0.442
430	0.380
440	0.217
450	0.142

A convenient method for the indirect determination of sulfate might be based on the precipitation of the sulfate with a slight excess of standard barium solution and the measurement of the excess by the above procedure. Another possible application of this new reagent might be for the estimation of lead, cerous cerium, or lanthanum, for these ions also yield slightly soluble precipitates.

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CORRESPONDENCE

Simultaneous Colorimetric Determination of Copper, Cobalt, and Nickel as Diethyldithiocarbamates

SIR: Further work by the author on the colorimetric determination of copper, cobalt, and nickel [Chilton, J. M., ANAL. CHEM., 25, 1274 (1953)] has resulted in several modifications to make the procedure more applicable to solutions containing large amounts of uranyl ions (25 to 50 mg. per ml.). The modified method has approximately twice the sensitivity of the original, with only a slight decrease in precision.

The changes made in the original procedure are as follows:

Take an aliquot of sample to contain one half the amount of metallic ions specified.

Use bromocresol green indicator instead of phenol red.

Use 15% sodium carbonate solution instead of ammonium hydroxide.

Extract only once with exactly 5.0 ml. of carbon tetrachloride, measured from a pipet, and drain directly into the spectrophotometer cell. Shake the separatory funnel vigorously for at least 3 minutes.

A saving of time may be accomplished in routine analyses by means of nomographs constructed from the simultaneous equations (Heacock, F. A., "Graphic Methods for Solving Problems," p. 81, Ann Arbor, Mich., Edwards Brothers, 1952).

Although most procedures specify the extraction of metal diethyldithiocarbamates from slightly basic solutions, no decrease in sensitivity was noted on lowering the pH of the aqueous solution to 4.0. The efficiency of a single extraction was lowered by the presence of ammonium ions. For this reason, and in order to form a soluble uranyl complex, sodium carbonate rather than ammonium hydroxide was used for neutralization.

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Direct Reading Emission Spectroscopy

AT THE Fifth Annual Conference of the American Association of Spectrographers, held May 7 at the Society of Western Engineers Building, Chicago, Ill., a Symposium on Direct Reading Emission Spectroscopy was presented. Abstracts of some of the papers are printed here.

Application of the Direct Reading Spectrometer for the Analysis of Low and High Alloy Cast Irons. L. E. HARPER, Campbell, Wyant & Cannon Foundry Co., Muskegon, Mich.

The general applicability of the direct reading spectrometer for the determination of silicon, manganese, chromium, nickel, molybdenum, copper, and vanadium in a variety of cast irons was presented. Included was a discussion of sampling techniques, source parameters, precision, accuracy, and reliability.

Analysis of High Alloy Steels. J. H. JURMAIN, Baird Associates, Inc., Cambridge, Mass.

This paper discussed recent results on high alloy steel analysis, the relative values of direct calibration *vs.* dilution computation, and factors found to be important from the standpoint of precision and accuracy.

Versatility of Direct Reading Spectrometer. L. W. MCNEIL AND A. F. ERNESTER, Ford Motor Co., Detroit, Mich.

The Baird direct reading spectrometer, which was originally designed for the analysis of ferrous alloys, has been successfully adapted to the analysis of other alloys whose matrix may be any one of several elements normally analyzed in ferrous materials.

Specific data were given regarding the procedure of change-over and the accuracy of results for the various matrix materials.

Determination of Metallic Elements in Nonmetallic Matrices. A. A. SHURKUS, Applied Research Laboratories, Glendale, Calif.

The determination of metallic elements in nonmetallic matrices has been studied using both emission spectroscopy and x-ray fluorescence. This paper compares the results obtained using these two supplementary methods.

Quantometric Determinations of Metallic Elements in Lubricating Oil Blends. P. A. ASSEFF AND L. L. GRIESHAMMER, Lubrizol Corp., Cleveland, Ohio.

The elements barium, zinc, phosphorus, calcium, and sodium in lubricating oils have been determined by quantometric analysis utilizing a rotating disk technique. Cadmium is used as an internal standard and magnesium is added to serve as a buffer. This is a rapid and precise method permitting the analysis of from 20 to 30 oils per day. Standard deviations of from 2 to 5% were obtained for barium, zinc, and phosphorus, and 5 to 10% for calcium and sodium. Sample preparation, excitation conditions, precision, and interfering elements were discussed.

Instrumental Flexibility of Direct Reading Instruments. J. L. SAUNDERSON, Baird Associates, Inc., Cambridge, Mass.

This paper is concerned with the solution to the instrumental problems encountered in designing versatile direct reading equipment which is to be used for a large variety of analytical problems.

New Multichannel Direct Reading Spectrograph. FREDERICK BRECH, Jarrell-Ash Co., Boston, Mass.

A multichannel direct reading spectrograph based on the Wadsworth mount was described. Spectra are displayed on two levels, on each of which several fixed-position exit slits and photomultipliers may be located. By this arrangement, two detector tubes may be sited on two lines with a small wave-length separation without the use of optical separator elements. With the circuits employed, the signal from each photomultiplier is converted to fixed amplitude pulses whose frequency is proportional to the signal strength. The working curve for each channel is displayed on a separate dial face, the rotation of which from a fiduciary position may be employed when necessary to compensate for a shift of the working curve. Details of the instrument and sample analyses performed with it were discussed.