region of 1 μg. of technetium. However, this blank, if not corrected for, nullifies a negative error at higher technetium levels, which is probably due to oxidation of the technetium(V) thiocyanate. Consequently, reasonably accurate results are obtained in the presence of a limited amount of nitrate.

Above 6% nitrate, the thiocyanate in the extract deteriorates too rapidly to permit accurate measurement of absorbance. Excessive amounts of nitrate can be removed (Table IV) by controlled evaporation to the first appearance of perchloric acid vapors. Solutions may be evaporated without loss of technetium if the temperature does not exceed 110° C. (*2*).

ACCURACY AND PRECISION

The accuracy and precision of the method were determined for 0.5 and 30 μg. of technetium (Table V). The slight errors are due to the uranium effect, as seen in Figure 7, and corrections may be applied accordingly.

Table V. Accuracy and Precision

(Samples—7.5 grams of hydrolyzed UF_6)

Tc Added, μg.	Tc Found[a], μg.	Number of Determinations	Mean Error, μg.	Std. Dev., μg.
0.00 (blank)	0.00	5	...	...
0.50	0.49	5	−0.01	±0.03
30.0	29.3	5	−0.7	±0.1

[a] Average values, using calibration curve prepared in absence of U.

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Use of 1,3-Dimethylvioluric Acid in Spectrophotometric Titrations of Alkali and Alkaline Earth Salts

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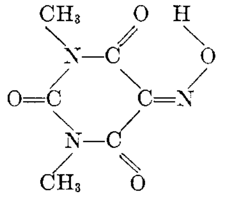
▶ A spectrophotometric study has been made of the lithium, sodium, potassium, rubidium, cesium, beryllium, and magnesium salts of 1,3-dimethyl-5-isonitrosobarbituric acid (1,3-dimethylvioluric acid, DMVA). The applicability of DMVA for the spectrophotometric titration of alkali and alkaline earth salts in aqueous solution has been investigated. These metals were determined with an accuracy that ranged from 1 to 10 parts per thousand in 0.01 to 0.0001*M* concentrations. At these concentrations the precision, expressed as standard deviation, ranged from 0.3 to 1.5%. Separation and thermal decomposition of potassium tetraphenylborate yielded water-soluble potassium borate which was titrated spectrophotometrically by DMVA.

Despite the fact that the reported colors and solubilities (*1*, *2*, *7*, *9*) of the salts of violuric acid, 5-isonitrosobarbituric acid, and 1,3-dimethylvioluric acid (DMVA) are extremely favorable for analytical purposes, so far they have found little use. Violuric acid was used by Muraca and Bonsack (*8*) to determine sodium colorimetrically at 605 mμ and by Erlenmeyer, Hahn, and Sorki (*5*) to detect the presence of lithium, sodium, potassium, beryllium, calcium, magnesium, and strontium in paper chromatography. No methods using DMVA were found in the literature.

The purpose of the present work was to investigate the feasibility of using DMVA as a titrant in the spectrophotometric titration of alkali and alkaline earth metals. DMVA is a monobasic acid that forms highly colored salts with some metals. In the case of the alkali and alkaline earth salts the maximum absorbance is at 538 ± 5 mμ. DMVA has the following structure:



EXPERIMENTAL

Equipment. All spectral measurements were made using the Beckman DU spectrophotometer. A Mallory battery charger, 6-AC-6 type, connected to a 110-volt a.c. line was used to charge and stabilize a 6-volt truck battery that was used as a power source. The tungsten lamp of the Beckman DU was used with the charger on.

The titrations were performed using a Microchemical Specialties Co. microcolorimetric cell compartment in place of the 1-cm. cell compartment of the instrument. By removing the bottom plate the compartment was enlarged to accommodate a 100-ml. Berzelius beaker. The knob was removed from the compartment cover; the bolt hole was enlarged to accommodate the tip of a 10-ml. microburet. The whole compartment was made light-tight by fitting a rubber grommet around the buret tip just below the cover. The buret was covered with black tape from the cover to the 10-ml. mark to prevent light leakage.

A 100-ml. Berzelius beaker was modified with a side arm near the bottom so the solution could be stirred by bubbling compressed nitrogen through the solution. The rubber tubing leading the nitrogen to the beaker

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was inserted through the hole left by the removal of the micrometer head from the microcolorimetric cell compartment. Vertical movement of the gas through the solution displaced all other dissolved gases and effectively stirred the solution.

Preparation of 1,3-Dimethylvioluric Acid. The Biltz (*3, 4*) method with modifications was used for the preparation of the acid.

A solution of 40 grams of caffeine in 175 ml. of slightly warm $6N$ hydrochloric acid was held at 50 to 55° C., and 16 grams of potassium chlorate were added during 1.5 hours. A precipitate of 8-chlorocaffeine soon formed only to redissolve about 5 minutes after all potassium chlorate had been added.

The clear solution was cooled in ice, and air was drawn through it for 2 hours. Then a solution of 23 grams of stannous chloride in 20 ml. of concentrated hydrochloric acid and 20 ml. of water were added dropwise to the ice cold solution during 30 minutes' time. Air was drawn through the solution for 2 more hours. During this time tetramethylalloxantin precipitated and then was collected on the filter, washed sparingly with water, and air dried.

Table I. Titrations of Alkali Metal Salts with 1,3-Dimethylvioluric Acid

µeq.			%
Taken	Found	% Found	Std. Dev.
	Potassium Carbonate		
43.1	43.0	99.5	
48.1	48.2	100.2	
	48.2	100.2	
	48.3	100.4	
	48.3	100.4	
	48.0	99.8	
52.1	52.2	100.2	
	52.0	99.9	
108.0	108.0	100.0	
	108.0	100.0	
		Av. 100.1	0.3
	Sodium Carbonate		
59.7	58.4	97.8	
	59.2	99.2	
	59.5	99.7	
	59.3	99.3	
		Av. 99.0	1.0
	Lithium Carbonate		
42.9	43.2	100.7	
	42.2	98.4	
	42.9	100.0	
	42.4	98.8	
	43.3	100.9	
	43.7	101.9	
	42.8	99.8	
57.7	57.3	99.3	
85.9	85.0	99.0	
		Av. 101.1	1.3
	Sodium Tetraborate		
21.1	21.2	100.4	
35.1	35.1	100.0	
52.7	52.2	99.0	
	52.4	99.6	
87.8	86.4	98.4	
	86.6	98.6	
	87.8	100.0	
	87.7	99.9	
	87.7	99.9	
		Av. 99.8	0.8

The tetramethylalloxantin was wetted slightly with water and then, with warming, was dissolved by adding 25 ml. of fuming nitric acid portionwise. Dimethylalloxan precipitated when the solution was cooled in the refrigerator. The precipitate was collected on the filter, washed sparingly with water, dissolved in a minimum of hot water, and 10 grams of hydroxylamine hydrochloride were added with heating. When the solution was cooled, 25.1 grams of 1,3-dimethylvioluric acid precipitated, m.p. 128° to 129° C. corr. Recrystallization from 95% ethyl alcohol yielded 24.0 grams of white product, m.p. 141.0° to 141.5° C. corr. (*6*).

Solutions. Primary standard solutions of 0.005- to $0.01N$ 1,3-dimethylvioluric acid were prepared for use as titrant.

Standard solutions were prepared of $0.004632N$ sodium acetate, $0.01847N$ potassium acetate, $0.01191N$ lithium acetate, $0.01756N$ sodium tetraborate, $0.002986N$ sodium carbonate, $0.001923N$ lithium carbonate, $0.02158N$ potassium carbonate, $0.00252N$ magnesium carbonate, $0.009203N$ beryllium carbonate, $0.04364N$ rubidium iodide, $0.07018N$ cesium chloride, and $0.01606N$ sodium sulfate.

Method. The titrations were made at a wavelength of 538 mµ, which represents very closely the maxima shown by the colored salt solutions. At this wavelength the molar absorptivity of the salt solutions ranged from 53.3 to 58.4 in distilled water. An aliquot of a standard solution, generally 5 ml., was measured into the titration vessel and diluted to 80 ml. with distilled water. This volume ensured that the liquid surface was well above the light beam and allowed room for the addition of 20 ml. of titrant. The nitrogen flow rate was adjusted to 2 bubbles per second, the compartment was closed, and the spectrometer was adjusted to give a zero absorbance reading. The aqueous solution of DMVA was added in 1-ml. increments. Mixing was very rapid and the absorbance was read immediately.

The absorbance was plotted against milliliters of titrant and the end point taken as the point of inflection. Plotting on large size graph paper reduced graphing errors.

RESULTS AND DISCUSSION

Aliquots of the standard solutions were titrated with DMVA. The results are recorded in Table I with concentrations expressed in microequivalents (10^{-6} eq.).

By titrating 5-ml. aliquots (48.1 µeq.) of the standard solution of potassium carbonate with DMVA at various times during a period of 9 days, the titrant was found to be stable for this time. These titrations not only served to test the stability of the DMVA solution but also to determine the precision of the titration. The average percentage of these experiments was 100.2 and the standard deviation was 0.2%.

Titrations with the same solutions after standing 4 weeks gave results about 10% higher, indicating slow decomposition of the acid solution over a long period of time.

During preliminary titrations of lithium carbonate with magnetic stirring the average percentage recovery decreased with increasing amounts of lithium carbonate. A low percentage was found whenever the amount of lithium carbonate taken exceeded 40 µeq. This effect could have been due either to failure of Beer's law at the higher concentrations or to a decrease in the absorbance because of a lowering of the pH caused by carbonic acid formation during the titration.

To test these effects DMVA was added in equivalent amounts to varying concentrations of lithium carbonate, and the absorbance for each of the solutions was measured. Carbon dioxide was bubbled through each solution for 2 minutes and the absorbance was measured again. Beer's law was obeyed in solutions to concentrations beyond 85.2 µeq. However, when the solutions were saturated with carbon dioxide, the absorbance readings were much less. When the same solutions were decarbonated by bubbling nitrogen through them, the absorbance values increased to the original values; that is, to the absorbances registered prior to carbonation. Thus, the decrease in percentages found at the higher lithium carbonate concentrations was due to a decrease in pH caused by an increase in carbonic acid and not from a failure of Beer's law. For this reason the solutions being titrated were decarbonated with bubbling nitrogen during titration.

To determine the end point of the titrations, absorbance was plotted *vs.* milliliters of titrant with correction made for dilution of the solution being titrated. The curves had an upward trend after the end point that was caused by slight absorbance of DMVA at the wavelength of titration. Subtracting the absorbance values of a blank titration from those of an actual titration produced a horizontal curve after the inflection. Correcting for the blank absorbance values was not necessary since the correction did not affect the end point within the limits of accuracy for this determination (Figure 1).

Magnesium and beryllium salts of weak acids gave colored solutions with DMVA. The results are given in Table II.

Alkali salts of strong acids cause little or no color formation in aqueous solutions of DMVA, but halides, nitrates, and sulfates can be converted to borates which are amenable to titration. Re-

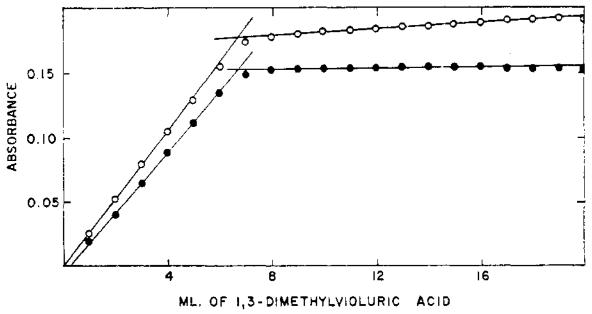

Figure 1. Titration of sodium tetraborate with 1,3-dimethylvioluric acid

52.7 μeq. of sodium, 0.007825*N* 1,3-dimethylvioluric acid
○ Uncorrected for absorption of acid
● Corrected for absorption of acid

Table II. Titrations of Alkaline Earth Salts with 1,3-Dimethylvioluric Acid

Compound	No. of Titrations	% Found (av.)	% Std. Dev.
$MgCO_3$	4	100.2	0.8
$BeCO_3$	9	99.8	0.8

Table III. Titration of Alkali Halides Converted to Borates

Compound	No. of Titrations	% Found (av.)	% Std. Dev.
RbI	6	100.2	1.2
CsCl	5	100.2	0.6
Na_2SO_4	4	101.5	1.5

sults of such titrations are given in Table III.

An aliquot containing 32 to 140 μeq. of alkali halide, nitrate, or sulfate was evaporated in a platinum crucible in an oven at 95° to 98° C. The salt residue was heated with excess boric acid crystals for 1 minute over a Meeker burner. The resultant borate was dissolved in 80 ml. of distilled water and was titrated.

Many alkali and alkaline earth salts in extremely small quantities can be titrated spectrophotometrically using 1,3-dimethylvioluric acid. Color development is general, and this lack of specificity limits the usefulness of the acid. As a general rule, to be useful the titration must be performed on a single salt.

Determination of Potassium. In studies of the thermal stability of potassium tetraphenylborate it was reported (*9*) that the salt was converted quantitatively to potassium metaborate by heating over the full flame of the Bunsen burner for 1 minute. The thermal decomposition of the same salt was reported (*10*) in a thermogravimetric study. It was believed that the thermal decomposition product was KBO_2. These studies suggested a new method for the determination of potassium by a spectrophotometric titration.

An aliquot (48.1 μeq.) of a potassium salt solution was measured into a beaker and was treated with 20 ml. of fresh sodium tetraphenylborate solution. The concentration of the sodium tetraphenylborate was such that there was approximately a 100% excess. To produce a crystalline precipitate suitable for filtration, 4 drops (0.2 ml.) of concentrated hydrochloric acid were added. The precipitate became crystalline after digesting 2 hours. The supernatent liquid was removed through a medium porosity filter stick leaving the precipitated potassium tetraphenylborate. The precipitate was washed with distilled water saturated with potassium tetraphenylborate and finally with distilled water.

The potassium tetraphenylborate was dissolved in acetone, and the filter stick was back-washed with the acetone. The combined acetone solutions were transferred to a platinum crucible and evaporated in an oven, leaving the potassium tetraphenylborate in the crucible. The dry precipitate was heated by a Meeker burner to red heat (about 600° C.) for 2 minutes, converting the potassium tetraphenylborate to potassium metaborate. After cooling, the potassium metaborate was dissolved in distilled water, transferred to the titration vessel, and made to a volume of 80 ml. It was titrated with standard 0.006 to 0.008*N* 1,3-dimethylvioluric acid at 540-mμ wavelength. Typical results are shown in Table IV.

Table IV. Titration of Potassium after Decomposition of Potassium Tetraphenylborate

Age of (hrs.)	μeq. Taken	μeq. Found
2	48.1	48.1
		48.1
		48.1
		48.1
3	48.1	48.1
		48.1
		48.1
		48.1

Two hours was sufficient to age the precipitate. The potassium tetraphenylborate was quantitatively converted to the soluble titrable salt by sufficient heating.

After the procedure was developed and the correct conditions established, the microequivalents found were in excellent agreement with the results found when the original potassium solution was titrated with 1,3-dimethylvioluric acid directly. The presence of ammonium ions apparently caused no error in the potassium values. One drop of ammonium hydroxide was added to the last two solutions. The ammonium was precipitated, but when the precipitate was heated it was volatilized.

Table V. Titration of Sodium Tetraborate and Potassium Carbonate with 1,3-Dimethylvioluric Acid

μeq. Na taken	μeq. K taken	μeq. Total	μeq. Found	% Found	% Std. Dev.
35.12	19.24	54.36	54.40	100.1	
			54.10	99.5	
			54.33	99.9	
			54.51	100.3	
			54.59	100.4	
			54.42	100.1	
			54.42	100.1	
			53.97	99.3	
			55.24	101.7	
			53.91	99.2	
			54.10	99.5	
			54.35	100.0	
35.12	14.43	49.55	49.41	99.7	
			48.82	98.5	
			49.48	99.5	
			49.12	99.1	
			49.55	100.0	
			49.69	100.3	
				Av. 99.9	1.1

Determination of Potassium and Sodium. In effect sodium and potassium can be determined in the presence of one another when they are present as the salts of weak acids. The total of the two can be determined on one portion of solution by titration with DMVA. The potassium can be precipitated with sodium tetraphenylborate on the same or a separate portion of the solution, converted to potassium metaborate, and titrated.

This was demonstrated experimentally by the results listed in Table V. The first twelve solutions used for the following titrations were made by pipetting a 2-ml. aliquot of sodium tetraborate solution (35.12 μeq.) into the titration vessel, followed by a 2-ml. aliquot of potassium carbonate (19.24 μeq.). Seventy-six milliliters of distilled water were added to the vessel and the solution was titrated. The last solutions were made by combining a 5-ml. aliquot of potassium tetraborate (14.43 μeq.) with 70 ml. of distilled water in the titration vessel.

SUMMARY

Solutions of the salts of 1,3-dimethylvioluric acid are highly colored, and while the reagent is nonspecific for the metals reported here, it can be used in spectrophotometric titrations to determine alkali and alkaline earth metals. Aqueous solutions of DMVA are colorless in the presence of alkali metal salts of strong acids, but conversion of this type of salt to metal borate by fusion with excess boric acid permits their titration. Furthermore, potassium can be determined uniquely in very small amounts by precipitating it as the tetraphenylborate salt followed by thermal decomposition, solution in distilled water, and titration with DMVA. The acid is used in the dual capacity of acid and indicator and is capable of determining very small amounts of metal salts.

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Spectrophotometric Determination of Vanadium with 2,6-Pyridinedicarboxylic Acid

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▶ A method is presented for the determination of vanadium in a mixture of diverse ions. 2,6-Pyridinedicarboxylic acid is used as the reagent for the complexation of vanadium as a soluble colored species which forms on addition of 30% hydrogen peroxide. The interference due to iron and titanium is avoided by the addition of fluoride ion. Although molybdenum does form a peroxide complex, it does not absorb at 430 mμ the wavelength of maximum absorbance for the vanadium-2,6-pyridinedicarboxylic acid complex. Transition metal ions other than vanadium do not form a colored complex with the reagent under the conditions used.

ALTHOUGH METHODS for the spectrophotometric determination of vanadium are not uncommon, most of the available procedures involve either an extraction of the colored species or the removal of metal ion interferences present, especially in the analysis of steel samples (*1*, *4–6*). Recent work by Hartkamp described the synthesis of a solid 2,6-pyridinedicarboxylic acid–vanadium complex (*2*). A study of 2,6-pyridinedicarboxylic acid with a number of metal ions, including those commonly found in steels, disclosed that vanadium alone forms the desired complex under the specified conditions. As a consequence, the vanadium-2,6-pyridinedicarboxylic acid system was investigated thoroughly, and a spectrophotometric procedure for vanadium was developed which requires neither extraction nor metal ion removal.

APPARATUS AND REAGENTS

All spectrophotometric measurements were made at 25° C. with a Beckman DU or a Bausch & Lomb Spectronic 505 spectrophotometer using 1-cm. matched silica cells. A Beckman Zeromatic pH meter was used for all pH measurements.

Table I. Stability of the Vanadium Complex

Time, Hours (after H_2O_2 Addition)	Absorbance
0.00	0.00
0.25	1.40
0.50	1.40
1.00	1.40
2.00	1.40
3.00	1.40
4.00	1.40
5.00	1.35
6.00	1.20
8.00	1.00

2,6-Pyridinedicarboxylic acid was synthesized according to the method of Hess and Wissing by the oxidation of 2,6-dimethylpyridine with potassium permanganate (*3*). The reagent was purified by vacuum sublimation yielding a white crystalline compound with a melting point of 226–7° C. (literature value 226° C.) (*3*).

A 0.01*M* stock solution of 2,6-pyridinedicarboxylic acid, stable for more than 8 weeks, was prepared by dissolution of a weighed amount of the reagent in deionized water.

A standard solution of vanadium was prepared from vanadyl sulfate and standardized by titration with potassium permanganate.

All other reagents were prepared from reagent grade chemicals.

RECOMMENDED PROCEDURE

Dissolve the sample containing vanadium by appropriate means and dilute to a known volume. Pipet an aliquot containing 5 to 50 mg. of vanadium into a 50-ml. volumetric flask and adjust to pH 2 to 4. Add 5 ml. of 48% hydrofluoric acid, 1 ml. of 0.01*M* reagent solution for each milligram of vanadium, 5 ml. of 30% hydrogen peroxide, and allow the color to develop for 15 minutes. Adjust