results using the Parr bomb indicated an average of 1.14 p.p.m. of Se, with a standard deviation of ±0.019; for the Schöniger flask, an average of 1.17 p.p.m. of Se, with a standard deviation of ±0.012.

Table VII compares neutron activation with fluorometric DAB method of analysis for several types of plant samples. The results obtained agree well on four of the six samples. Duplicate results were not available on the neutron activation analyses.

Plant Samples. Table VIII shows the analytical results for Se in a number of diverse plant materials.

In this group of analyses alfalfa samples, from ranches where white muscle disease is prevalent, fall below 0.20 p.p.m. of Se; results from all nonwhite muscle ranches except one were greater than this value. These samples were taken some years ago before the use of bore-type hay samplers became prevalent; it is not certain how representative the samples are.

Animal Samples. Table IX shows the preliminary results obtained on a variety of animal samples. This type of analysis is being continued in our current white muscle research.

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Table IX. Fluorometric Determination of Selenium in Animal Tissues and Secretions

	Cattle[a] duplicates, p.p.m.		Sheep[b] duplicates, p.p.m.		Rat[b] duplicates, p.p.m.	
Liver[c]	2.24	2.25	1.98	1.98	2.03	2.13
Muscle[c]	3.25	3.30	2.49	2.31	1.29	1.64
Brain[c]	2.64	2.49	1.42	1.75	1.92	2.00
Heart[c]	2.35	2.30	1.28	1.28	2.66	2.84
Kidney[c]	0.63	0.61	3.19	3.10	2.65	2.63
Serum[d]	0.017	0.019				
Milk[d]	0.027	0.029				

[a] Parr bomb combustion.
[b] Schöniger flask combustion.
[c] Measured on dry basis.
[d] Measured on "as received basis."

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Determination of Water and Alkali Metal Oxide in Alkali Metal Salts of Selenium and Tellurium by Karl Fischer Titration

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▶ The moisture content or water of crystallization in alkali metal salts of selenium and tellurium can be determined accurately with the Karl Fischer reagent. Sodium selenite, potassium tellurite, and sodium tellurate behave like a mixture of the respective oxides, and the alkali metal oxide in these salts reacts quantitatively with the Karl Fischer reagent. The results for the alkali metal oxide content offer an indirect method for the determination of combined selenium or tellurium. Anhydrous sodium selenate is not affected by the reagent. The data obtained compare favorably with analyses of weight loss by thermal drying and of selenium or tellurium by potentiometric titration.

A GROWING interest is evidenced in the application of the Karl Fischer reagent in the inorganic field. Bryant *et al.* (*3*) studied the behavior of 25 hydrated inorganic salts and concluded that the Karl Fischer method is more rapid and precise than thermal drying procedures. In addition, base metal oxides, either free or as hydroxides or salts of weak acids, are the most frequent type of interfering materials, since water is formed by the action of these oxides upon hydroiodic acid. In general, since the interference is stoichiometric, it is possible to calculate the water content where the reaction is known.

This paper demonstrates the application of the Karl Fischer reagent to the alkali metal salts of selenium and tellurium. Both the water content and the alkali metal oxide content can be determined, with an indirect estimation of combined selenium or tellurium.

EXPERIMENTAL

Preparation of Samples. Sodium selenite was prepared by neutralizing a selenious acid solution with a slight excess of sodium hydroxide. A snow-white precipitate was formed on evaporating the resulting solution and anhydrous sodium selenite was obtained by drying the product to constant weight in a vacuum desiccator over potassium hydroxide. Sodium selenite pentahydrate crystals were obtained by allowing a saturated sodium selenite solution to stand at room temperature for about one month. Sodium selenate decahydrate crystals, snow-white, were obtained from technical grade sodium selenate by recrystallization. This operation was carried out at temperatures below 40° C. to avoid the formation of lower hydrates.

Potassium tellurite was prepared from tellurium dioxide and potassium hydroxide by following the same procedure as for the preparation of sodium selenite. Anhydrous potassium tellurite was obtained by oven-drying the product at 105° C. to constant weight.

Table I. Anhydrous Salts

Compound	% Na_2O (or K_2O) Found	Calcd. from Se or Te analyses	Theoretical
Na_2SeO_3	35.91 36.05 35.89	35.90	35.86
K_2TeO_3	37.05 37.03	...	37.11
$Na_2H_4TeO_6$	22.70 22.55	22.55	22.66

Potassium tellurite dihydrate, colorless crystals, was obtained from the alcohol layer upon adding ethyl alcohol to a saturated solution of potassium tellurite and allowing to stand for about one month. Disodium tetrahydrogen tellurate dihydrate, $Na_2H_4TeO_6 \cdot 2H_2O$, was prepared by Fouasson's method (*4*). The product was dried in air. Anhydrous disodium tetrahydrogen tellurate was obtained by drying the dihydrate at 50° C. to constant weight.

Preparation of Karl Fischer Reagent. The reagent was prepared following reported procedures (*1*, *6*).

Standardization of Reagent. The standardization was performed one week after the reagent had been prepared. In the first half of the present work, the reagent was standardized against a standard solution of water in methanol. In the second half, the reagent was standardized against sodium acetate trihydrate as recommended by Roy and Mabon (*5*).

Analytical Procedure. A sample (0.1 to 0.4 gram) equivalent to 2 to 4 mmoles of water was suspended in 25 ml. of anhydrous methanol in a 100-ml., glass-stoppered volumetric flask. Then the sample was titrated with standard reagent until the pale yellow of the liquid was permanently tinged reddish brown with free iodine. The water content of the suspending methanol was determined by a blank titration and the titer of the sample was corrected by this amount. (The selenium and tellurium salts are insoluble in methanol, and the reaction rate and the sharpness of the end point are dependent on the particle size of the sample. The time required to complete one titration is usually less than 30 minutes. In all samples, except sodium selenate, a dark-gray metallic selenium or tellurium precipitate was formed during the titration. Since the precipitate settled out readily, there was very little interference in the detection of the end point.)

Table II. Hydrated Salts

(Powder form)

Compound	% Na_2O (or K_2O) Found[a]	Calcd. from Se or Te analyses	% H_2O Found[a]	Found[b]	From wt. loss on drying	H_2O/anhyd. salt, mole ratio, x
$Na_2SeO_3 \cdot xH_2O$	30.92 31.01	...	13.77	...	13.90 (dried in vacuum desiccator over KOH overnight)	1.5
$K_2TeO_3 \cdot xH_2O$	30.86 30.99 31.10	30.74	16.86 16.50 16.20	16.86 16.52 16.20	16.25 (15 days at 105° C.)	2.8

[a] Calculation based on Method A.
[b] Calculation based on Method B.

RESULTS AND DISCUSSION

Typical data on the determinations of alkali metal oxide and/or water in sodium selenite, sodium selenate, potassium tellurite, and disodium tetrahydrogen tellurate are given in Tables I, II, and III. The calculation of the results was based on the following stoichiometric reactions. The salt-forming function of pyridine has been ignored in order to simplify the equations.

$$H_2O + I_2 + SO_2 + CH_3OH \rightarrow 2HI + HSO_4CH_3 \quad (1)$$

$$Na_2SeO_3 + I_2 + 3SO_2 + 3CH_3OH \rightarrow 2NaI + Se + 3HSO_4CH_3 \quad (2)$$

$$Na_2SeO_4 + I_2 + SO_2 + CH_3OH \rightarrow \text{no reaction within 24 hours} \quad (3)$$

$$K_2TeO_3 + I_2 + 3SO_2 + 3CH_3OH \rightarrow 2KI + Te + 3HSO_4CH_3 \quad (4)$$

$$Na_2H_4TeO_6 + 3I_2 + 6SO_2 + 6CH_3OH \rightarrow 2NaI + 4HI + Te + 6HSO_4CH_3 \quad (5)$$

In many cases, parallel potentiometric determinations of selenium or tellurium content (*2*), as well as deter-

Table III. Hydrated Salts

(Crystal form)

Compound	% Na_2O (or K_2O) Found[a]	Calcd. from Se or Te analyses	Theor.	% H_2O Found[a]	Found[b]	From wt. loss on drying	Theor.
$Na_2SeO_3 \cdot 5H_2O$	23.59 23.74 23.50	23.50	23.59	34.20 33.75 34.65	34.13 33.74 34.54	34.45 (2 days at 105° C.)	34.22
$Na_2SeO_4 \cdot 10H_2O$	...	16.73	16.80	49.50 49.50 49.45 49.60	...	49.18 (2 days at 105° C.)	48.78
$K_2TeO_3 \cdot 2H_2O$	32.29 32.59	...	32.48	12.96 12.11	...	12.54 (2 days at 105° C.)	12.41
$Na_2H_4TeO_6 \cdot 2H_2O$	20.00 20.00	19.89	20.02	11.75 11.75	11.83 11.82	12.11 (3 days at 50° C.)[c]	11.63

[a] Calculation based on Method A.
[b] Calculation based on Method B.
[c] Temperature recommended by Fouasson (*4*).

minations of the water content by thermal drying, were made. The results are given for comparison.

The results given in Table I indicate that the anhydrous salts of sodium selenite, potassium tellurite, and disodium tetrahydrogen tellurate react quantitatively with Karl Fischer reagent by following Reactions 2, 4, and 5, respectively. Hence, it is possible to calculate the water content of the hydrated salts. It is clear that the titer for the hydrated salts is a measure of the combined alkali metal oxide and water content. The latter, in this case, was calculated by two methods: Method A, assuming the sample is composed of pure anhydrous salt and water only; and Method B, estimating the alkali metal oxide content from separate selenium or tellurium analyses, then obtaining the water content from the titer by difference.

The calculated results are compared with the water content found from weight loss on thermal drying. The two sets of data agree very well, as shown in Tables II and III, although the thermal drying procedure is more time-consuming.

Sodium selenate is not affected by the Karl Fischer reagent and the titer is derived exclusively from water content. This is in line with Bryant *et al.* (*3*), who found that the normal and acid alkali salts of sulfuric acid are not affected by the Karl Fischer reagent.

The sulfur dioxide, present in the Karl Fischer reagent, reduces Se(IV), Te(IV), and Te(VI) in sodium selenite, potassium tellurite, and disodium tetrahydrogen tellurate, respectively, to metallic selenium and tellurium during the titration. No redox reactions take place between iodine and the selenium or tellurium species.

The nonintegers of the H_2O/Na_2SeO_3, and H_2O/K_2TeO_3 mole ratios in the case of the powder-form salts either represent the average number of moles of water of crystallization, or indicate that some of the water present is adsorbed on the surface of the solids. The preparation of potassium tellurite dihydrate crystal, $K_2TeO_3 \cdot 2H_2O$, has not been described in the literature previously.

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Determination of Phosphorus in Iron and Steel with Quinoline Molybdate

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▶ An improved method for volumetric or gravimetric determination of phosphorus in all classes of iron and steel is based on precipitation of phosphorus as quinoline phosphomolybdate from a perchloric–hydrochloric acid solution after oxidation to orthophosphate by refluxing with perchloric acid. Modifications overcome interference by iron, arsenic, zirconium, niobium, tantalum, and tungsten. Inhibition of precipitation by iron is overcome by adding more reagent or digesting the mixed solutions; of quinoline arsenomolybdate, by volatilization of arsenic with hydrobromic acid. Niobium, tantalum, and tungsten occlude phosphorus with their oxides, which are precipitated as the perchloric acid solution is taken to reflux. Zirconium phosphate is simultaneously precipitated. Phosphorus is recovered from these precipitates. Precipitation of zirconium phosphate later is avoided by stopping evaporation of the hydrobromic–perchloric acid solution as bromine ceases to be evolved. Precipitation of quinoline niobio- and tantalomolybdates from small amounts remaining in solution after perchloric acid reflux is prevented by addition of tartaric and nitric acids. Further precipitation of tungsten oxide with occlusion of phosphorus is also prevented by tartaric acid. Tests on NBS samples and current alloy types of iron and steel have established reproducibilities of ±0.001, ±0.002, ±0.01, and ±0.03 for phosphorus levels of 0.01, 0.1, 0.5, and 1.5%.

American, Australian, and British standard methods for phosphorus in iron and steel (*2*, *4*, *5*) have deficiencies which can be grouped into those affecting the time-length of the procedure and accuracy. The first group includes the necessity for supplementary oxidation of phosphorus, recovery of phosphorus from precipitated oxides, and conversion of ammonium phosphomolybdate (AmPMo) to magnesium ammonium phosphate (*2*) or lead molybdate (*4*, *5*) when a gravimetric measurement is desired.

The second group includes the gravimetric determination of small contents of phosphorus by the magnesium ammonium phosphate method (*2*). This may not give the accuracy desired because of limitations imposed by the low factor weight for phosphorus in magnesium pyrophosphate.

The presence of sulfuric acid, derived from sulfurous acid added to dissolve precipitated manganese oxides formed from the use of potassium permanganate for supplementary oxidation (*2*), may affect the yield. Small amounts of sulfuric acid increase the yield and large amounts decrease it when phosphorus content is measured volumetrically. The effect is negligible for small phosphorus contents, when the technique of dropwise addition of reagents is used to avoid excess. It becomes noticeable, however, when high phosphorus contents are determined and 10-ml. volumes of potassium permanganate and correspondingly large amounts of sulfurous acid are used—for example, Sections 31 and 39, ASTM methods for phosphorus in ferrous materials (*2*).

The standard methods yield low results for phosphorus contents of the order of 0.01%, because of the inhibiting effect of iron, and is not overcome by increasing the reagent addition to twice the usual amount and/or by standing for a long time. Yields of 0.004, 0.003, and 0.007% phosphorus by the standard methods for NBS samples 55a,