TABLE I. ANALYSES FOR CARBON MONOXIDE

(Rollefson and Grahame, *3*, found 49 ± 0.3%)

Sample *Cu. mm.*	Residue *Cu. mm.*	CO %
112.2	56.6	49.6
327	162.4	50.3
313	159.0	49.2
69.8	35.0	49.9
190.8	95.5	49.8
479	245	48.8

of carbon monoxide, the method should be applicable to any analysis in which liquid reagents may be avoided.

A few typical analyses for carbon monoxide are shown in Table I. No attempt has been made to improve the results obtained, but it is believed that increased time of preliminary evacuation and removal of water vapor would lead to improved performance.

There are a number of possible designs that may be applied to the reaction chamber to increase the versatility of the apparatus. For example, ground joint *L* could be replaced by a spherical ground joint, its female section being connected to stopcock *C*. The male section would have any desired number of indentations on its ground surface, within which could be attached pellets of the same or various reagents. In the first case, this would enable the reagent to be renewed merely by exposing a different indentation to the reaction chamber. In the second case, should the gas contain a number of components, reagents for removing only certain components could be exposed to the reaction chamber as desired. It is also possible that an explosion, a combustion, or an oxidation reaction chamber may be designed for the apparatus.

Acknowledgment

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Separation of Calcium Nitrate from Strontium Nitrate

By Monobutyl Ether of Ethylene Glycol

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IN SEPARATING and identifying barium, calcium, and strontium after these elements have been precipitated as carbonates, use is made of the differential solubilities of the salts of the alkaline earths or the selective solubilities of organic reagents on the anhydrous chlorides or nitrates of these metals. While the different procedures have given fairly satisfactory separation of the three alkaline earths, they have not offered a clear-cut and positive separation. The uncertainty has been especially marked with students in analytical chemistry and with the analyst who does not have occasion to make frequent separations of the alkaline earth metals.

Although the differential solubilities of the alkaline earth salts cannot be changed appreciably by varying the concentration of the separating reagents, the selective solubility of organic reagents on the anhydrous chlorides or nitrates should afford a positive separation if a reagent could be found which had a high solvent action on, say, the nitrate of calcium and a negligible, or exceedingly low, solvent action on the nitrate of strontium.

Anhydrous alcohol-ether mixtures (*4*), isopropyl alcohol (*2*), amyl alcohol (*3*), acetone (*5*), butyl alcohol (*6*), etc., have afforded a fair separation of the anhydrous chlorides or nitrates of the alkaline earths. However, the ether-alcohol mixture is rather dangerous on account of its easy inflammability. With these organic solvents the anhydrous solvent must be prepared and protected from the moisture of the atmosphere and should be used without moisture contact in order to keep the selective solvent action at a maximum-minimum ratio. Even then, these reagents do not give a complete separation of the anhydrous chlorides or nitrates of the alkaline earths.

An investigation of other solvents was undertaken, and the monobutyl ether of ethylene glycol (butyl Cellosolve) was found to have the desired properties. This reagent gives a complete separation of the anhydrous nitrates of strontium and calcium and, their hydrated nitrates are rendered anhydrous at, or below, the boiling point of the solvent (170.6° C.). Furthermore, the anhydrous solvent is obtained by heating it to the boiling point when dehydrating the calcium and strontium nitrates—that is, the calcium and strontium nitrates and the solvent are rendered anhydrous in one operation. Because of this double action, it is not necessary to dehydrate the nitrates by heating them at uncertain temperatures, and then attempt to dissolve the more soluble nitrate by triturating the baked nitrates in the solvent which is absorbing moisture from the air as well as from the vessel in which the salts were dehydrated.

The Reagent

Commercial butyl Cellosolve having a boiling range from 163° to 174° C. was used. About 96 per cent distills below 172°. It is water-white, somewhat hygroscopic, soluble in water in all proportions, does not have an unpleasant odor, is not easily ignited, but will burn when vaporized into a flame. The pH of the material used was 5.8. The inflammability does not appear to be dangerous or explosive, when the solvent is used as directed. The vaporized Cellosolve should be ignited when it is boiled off.

Semimicroprocedure for Analysis of Alkaline Earth Group

The alkaline earth group will be contained in the filtrate from the previous group precipitation. This filtrate will be ammoniacal and will contain ammonium sulfide.

Add 1 drop of neutral red indicator (pH 6.8 to 8.0) and boil the solution until it turns from yellow to red and becomes clear. [On boiling, the decomposition of the ammonium sulfide results in a deposit of sulfur (white), but when the solution becomes distinctly red, the white deposit disappears, and the solution becomes clear.] Make the volume of the filtrate to about 2 ml. by

PRECIPITATE: $BaCO_3$, $CaCO_3$, and $SrCO_3$. Treat the precipitate with a few drops of dilute acetic acid and wash the filter with 1 ml. of water. To the filtrate add 2 drops of a saturated solution of ammonium acetate and 2 drops of 1 *N* potassium chromate reagent. Shake the tube; if a precipitate is formed filter and wash the precipitate with water. [The precipitate should be washed with 3 to 5 ml. of water. Collect about 0.5 ml. of this water in the filtrate and discard the remainder.]

PRECIPITATE: $BaCrO_4$. Dissolve in 1 ml. of 0.1 *N* HCl. Add 1 drop of formalin solution, place the tube in the hot water bath, add several drops of a saturated solution of calcium sulfate. A white precipitate confirms the presence of barium. [The formaldehyde reduces the CrO_4^{--} (yellow) to Cr^{+++} (green) and enables one better to observe the formation of the white ($BaSO_4$) precipitate.]

FILTRATE: calcium and strontium ions. Add 1 drop of neutral red indicator and then concentrated ammonium hydroxide until the solution is yellow. To this yellow solution add 5 drops of 1 *N* sodium carbonate reagent. Place the tube in the hot water bath until the precipitate has settled. Filter and wash the precipitate with water to which a drop of sodium carbonate has been added.

PRECIPITATE: $CaCO_3$ and $SrCO_3$. Dissolve in a drop or two of dilute nitric acid and wash the filter with about 1 ml. of water. Evaporate the filtrate to incipient dryness by use of the burner flame. [Do not evaporate to complete dryness—i. e., avoid overheating the calcium and strontium nitrates.] To this practically dry residue add 10 drops of butyl Cellosolve, and again evaporate to incipient dryness. To the residue add 1 ml. of butyl Cellosolve and bring to boiling. Filter the hot solution (caution) through a dry filter (*) medium, glass or cotton (*1*). Add to the test tube another milliliter of butyl Cellosolve; heat to boiling and filter through the same filter which was just used.

FILTRATE: $Ca(NO_3)_2$. Add 1 drop of oxalic acid reagent. A white precipitate shows the presence of calcium.

RESIDUE: $Sr(NO_3)_2$. To the residue add 1 ml. of water and filter through (*) above. To the filtrate add 2 drops of ammonium sulfate reagent. Place the tube in the hot water bath and allow to stand for a few minutes. A white precipitate confirms the presence of strontium.

adding or boiling off water. Add 1 drop of concentrated ammonium hydroxide and 5 drops of 2 *N* ammonium carbonate reagent. Place the tube in the hot water bath until the precipitate has settled (*1*). To the clear solution above the precipitate add 1 drop of ammonium carbonate. If a precipitate appears in the clear solution, add ammonium carbonate until precipitation is complete. Filter and wash the precipitate with water to which a drop of ammonium carbonate has been added. (See above.)

Solubilities

Table I gives comparative solubility (grams per ml.) of a few common salts of the alkaline earths in water and of the anhydrous nitrates in butyl Cellosolve. The solubility of the anhydrous nitrates of barium, calcium, and strontium is based on the following procedure.

A drop of a 0.1 *M* solution of barium and strontium nitrates was boiled in about 1 ml. of the reagent until the salt and the reagent were rendered anhydrous. (This is accomplished before the reagent is entirely evaporated.) To the anhydrous salt 5 ml. of the reagent were added and brought to boiling. The hot reagent was filtered through a dry filter medium (glass wool), 1 ml. of the filtered reagent was evaporated to dryness, the residue was dissolved in 1 ml. of water, and to this solution a drop of ammonium carbonate for strontium and a drop of ammonium sulfate for barium were added. No precipitate was noticeable in either test after allowing to stand for 5 minutes. Attempts to determine the solubility by evaporating 10 ml. of the anhydrous reagent, which had been saturated with anhydrous barium and strontium nitrates, and weighing the residue gave very low but variable and uncertain results. This appeared to be due to a slight decomposition of the reagent on evaporation which resulted in some carbon deposits.

The solubility of the anhydrous calcium nitrate was determined by saturating the anhydrous reagent with the anhydrous calcium salt, evaporating 1 ml. of the clear, saturated reagent to dryness, and weighing the residue.

TABLE I. SOLUBILITIES OF ALKALINE EARTH SALTS

	Barium	Calcium	Strontium
Carbonate	2.2×10^{-5}	1.5×10^{-5}	1.1×10^{-5}
Chromate	3.4×10^{-6}	1.6×10^{-1}	1.2×10^{-3}
Oxalate	9.3×10^{-5}	6.7×10^{-6}	5.1×10^{-5}
Sulfate	2.3×10^{-6}	2.4×10^{-3}	1.1×10^{-4}
Nitrate (in butyl Cellosolve)	Not more than 2.3×10^{-6}	2.43×10^{-1}	Not more than 1.1×10^{-5}

Summary

Calcium nitrate is completely and easily separated from strontium nitrate by the use of the monobutyl ether of ethylene glycol. The hydrated calcium and strontium nitrates and the reagent are rendered anhydrous by boiling the nitrates in the reagent (b. p. 170.6° C.).

The solubility of anhydrous calcium nitrate in the reagent is 2.43×10^{-1} gram per ml., while the solubility of the anhydrous barium and strontium nitrates in the anhydrous reagent is not more than that of strontium carbonate and barium sulfate in water.

An analysis of 25 unknowns of the alkaline and alkaline earth groups, using 1 drop of the unknown solution of 0.1 *M* concentration, gave results 100 per cent correct, and without uncertainty as to the presence or absence of the alkaline earth metals.

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