

Tables V and VI show the results of the analysis of three commercial preparations of progesterone in oil and 12 commercial samples of testosterone propionate in oil without chromatographic separation from the oil. A few of the testosterone propionate samples at each concentration level were analyzed also using the chromatographic technique. For comparison, the progesterone samples were analyzed also by a slight modification of the U. S. Pharmacopeia XIV method for progesterone injection (9, 11), and the testosterone propionate samples by the semicarbazide method of Madigan, Zenno, and Pheasant (7) and by the bioassay method of the U.S.P. XIV for testosterone propionate injection (12). The author experienced great difficulty in filtering the semicarbazones formed in the semicarbazide method, and the results in many of the cases are probably high.

Identification of Testosterone Propionate in Oil. Because the isonicotinyl hydrazone of testosterone propionate could be purified easily, a technique was developed for the identification of testosterone propionate in oil solutions. A quantity of oil containing 25 mg. of testosterone propionate and 50 mg. of isonicotinic acid hydrazide were added to 5 ml. of an acid-alcohol mixture containing 1.25 ml. of concentrated hydrochloric acid per 100 ml. of absolute alcohol. The mixture was refluxed on the steam bath for 15 minutes. After cooling, the mixture was diluted with 25 ml. of ether. The precipitated hydrochlorides of isonicotinic acid hydrazide and the hydrazone of testosterone propionate were collected on a coarse sintered-glass filter and washed with 15 ml. of ether. The residue was transferred to a

separatory funnel with 10 ml. of water and 10 ml. of chloroform. After shaking and separating the layers, the aqueous layer was washed with 5 ml. of chloroform. The combined chloroform solutions were washed three times with 5-ml. portions of water, filtered, and evaporated to dryness. The residue was recrystallized once from 50% ethanol. After drying, the hydrazone melted at 192° to 4°C.

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Determination of Carbon in Sodium-Potassium Alloy

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Carbon contained in sodium-potassium alloy, one of the heat exchange media being considered for use in nuclear reactors, can seriously weaken stainless steel container material by carburizing the steel to an appreciable depth. The method described was developed for determining the carbon content of sodium-potassium alloy being used in heat transfer studies. The method developed for this purpose is a modification of the microcombustion procedure and involves the ignition of a 100-mg. sample to convert any carbon present to carbon dioxide which can then be absorbed and weighed. Analytical results are accurate to within tolerances acceptable in microcombustion analysis. The method described also covers the problem of sampling hot sodium potassium alloy from dynamic systems, and the transfer of the sample from the sampling site to the specially designed analytical equipment.

CAREFULLY controlled tests have demonstrated that the 25-20 and 18-8 type alloys can be quickly carburized to an appreciable depth when in contact with sodium-potassium alloy to which carbon has been added. Carburization of the alloys of construction weakens these materials, especially under impact loads. Therefore, it became necessary to develop a method for determining the carbon content of sodium-potassium alloys (hereafter referred to in the text as NaK) so that the carbon content could be ascertained before the liquid alloy was used for filling a given system.

A literature survey revealed little positive information regarding analytical procedures for carbon impurities in the alkali metals. However, in considering the classical method of carbon determination by microcombustion, it was felt that the most promising approach to the NaK carbon problem lay in some

modification of the method which has been in use since the time of Pregl (6).

It was obvious from the start that considerable revision of the conventional micromethod would be necessary before it could be adapted to NaK analysis. The very nature of this reactive material required completely different methods of sampling, weighing, and introducing of the sample into the combustion tube.

The sampling and analytical methods described below have been proved to be quite satisfactory. Total time required for an analysis is comparable with that for regular carbon microanalysis, but the number of details needing attention during an analysis is considerably larger. The combustion tube in particular, and the attendant apparatus in general, gets more severe usage than do conventional combustion trains. The result is that more than the usual amount of maintenance time is required.

ANALYTICAL APPARATUS

The analytical apparatus will be considered in three parts: the gas purification systems, the sample introduction apparatus, and the combustion tube. A diagram and over-all photograph of the completely assembled combustion train are shown in Figures 1 and 2.

Gas Purification Systems. To obtain oxygen of sufficient purity, cylinder oxygen, at a regulated low pressure, is passed through an absorption train of Ascarite, Drierite, phosphorus pentoxide, and hot copper oxide, followed by a micro bubble counter and Ascarite-Drierite U-tube. The capacity of the train is designed to effect purification of the oxygen flowing at a rate in excess of the 20 cc. per minute which are required at the initial moment of NaK ignition. The purified oxygen enters the combustion tube via side arm O (Figure 1).

Chemically pure nitrogen is obtained by passing cylinder nitrogen of prepurified grade through a pressure reducing valve, from

which it passes through a tube of hot degreased copper turnings followed by an absorption train similar to that used for removing impurities from the oxygen stream. The purified nitrogen enters the sample introduction apparatus portion of the combustion train via side arm *N* (Figure 1). Constant pressure in the nitrogen purification system is safeguarded by a mercury bubbler-type release tube.

A separate air purification system is used to provide air for flushing the oxygen out of the absorption tubes before each weighing. Compressed air supplied from a bench outlet is passed through a trap to remove oil, and then through ascarite and drierite of sufficient amount to remove all carbon dioxide and water. Pressure in the air purification system is regulated by a standard micro pressure regulator.

Combustion Tube and Sample Introduction Chamber. Generally, in microcombustion work, introducing the sample into the combustion tube presents no problem. This phase of NaK analysis, however, required the use of special apparatus and procedures.

The combustion tube (Figure 3) is made of transparent quartz. Its design is similar to that of standard microcombustion tubes except for an enlarged combustion chamber designed to accommodate larger sample boats than are used for conventional micro-combustions (5).

In order to introduce NaK samples into the combustion chamber without exposure to the atmosphere, a sample introduction chamber (Figure 4) was added to the combustion tube at the enlarged end. This introduction chamber is attached to the combustion tube via a 34/28 joint and consists of a 20-mm.-bore, hollow blown stopcock (Figure 1) sealed to a large borosilicate glass tube. This large stopcock serves to separate the inert (nitrogen) atmosphere of the introduction chamber from the oxygen atmosphere of the combustion chamber. A side arm is provided on each side of the stopcock for introducing nitrogen into the introduction chamber and purified oxygen into the combustion chamber. The end of the tube on the introduction side of the stopcock is provided with a 34/28 joint used for attaching either the cap (Figure 4), or the sampler stopcock (Figure 5).

A "push-pull rod" is used for manipulating sample boats in the combustion train. One end of the rod is flattened into a disk and the other end encloses a section of steel rod. The "push-pull rod" is enclosed in a glass tube housing provided with an 18/8 ball joint by means of which it can be attached to either the cap on the introduction chamber, or the sampler stopcock. The other end of the housing is closed except for a 2-mm. hole. By using a magnet external to the housing, the rod can be moved back and forth for manipulating sample boats in the closed system.

The filling of the main (11-mm. outside diameter) section of the combustion tube (Figure 3) is similar to the universal filling of microcombustion carbon-hydrogen tubes (2, 4, 6). The platinum gauze roll is omitted, however, and a large loose asbestos plug is placed in the 30-mm. outside diameter tube at the constricted end against the copper oxide filling. The purpose of this plug of asbestos is to ensure exposure of the volatilized sample to a heated surface so that the sample will be thoroughly ignited; otherwise vaporized NaK may be carried into the combustion tube filling which is maintained at a lower temperature level and where thermal decomposition of carbonates would be questionable.

To protect the ignition section of the quartz tube against the fluxing action of hot alkali, a loosely fitting, thin-walled, transparent quartz sleeve, 100 mm. long and open at both ends, is inserted into the combustion chamber against the large plug of asbestos. This protective sleeve is expendable and can readily be replaced as frequently as conditions demand.

The sample and large asbestos plug in the ignition chamber are heated

by two air-gas, blast-type Fischer burners to a final temperature of 950° C. or above. The section of the combustion tube filled with copper oxide is maintained at 700° C. in a micro-tube furnace, and the section filled with lead peroxide is heated by the ordinary type microcombustion mortar heater maintained at 180° C.

Portions of the combustion train adjacent to the blast burners can be satisfactorily protected against the high ignition temperatures by using a thin slab of refractory brick placed on either end of the 100-mm.-long sample ignition area. The refractory next to the tube furnace should be backed by a sheet of asbestos paper. The other refractory is backed by a 1-inch-thick sheet of insulation block to protect the borosilicate glass sample introduction apparatus from the heat of the burners. A cooling air jet directed against the standard taper joint between the introduction apparatus and combustion tube supplements the protection afforded by the refractory brick and insulation block.

The absorption tubes used are the usual straight-type Drierite and Ascarite microabsorption tubes. A Mariotte flask is used for assisting in the control of the flow of combustion products through the packed section of the combustion tube and absorption tubes.

REAGENTS

Oxygen, supplied from a cylinder of compressed oxygen of 99.8% purity.

Nitrogen, prepurified grade (99.99% pure) from a compressed gas cylinder.

Sulfuric acid, concentrated reagent grade.

Sulfuric acid, 10% solution by volume.

Magnesium perchlorate, anhydrous granular.

Ascarite, 8-20 mesh.

Copper oxide, reagent grade, wire form, preignited in an atmosphere of oxygen.

Lead peroxide, Special-Micro grade, 12-20 mesh.

Phosphorus pentoxide, reagent grade.

Copper metal, light, degreased turnings.

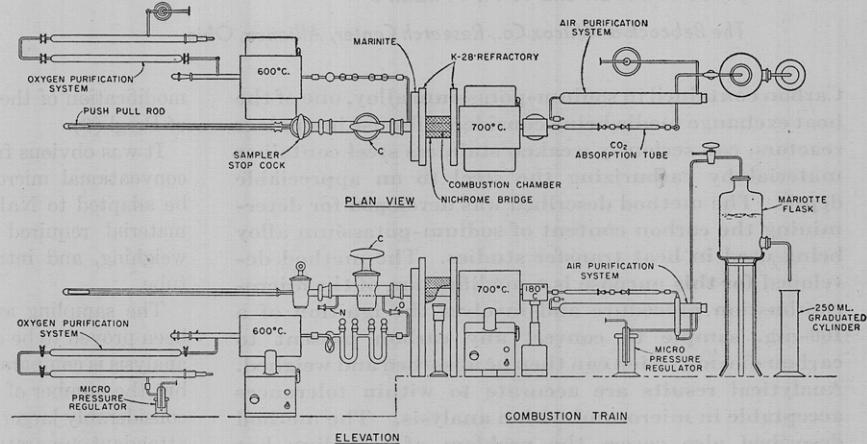


Figure 1. Combustion train

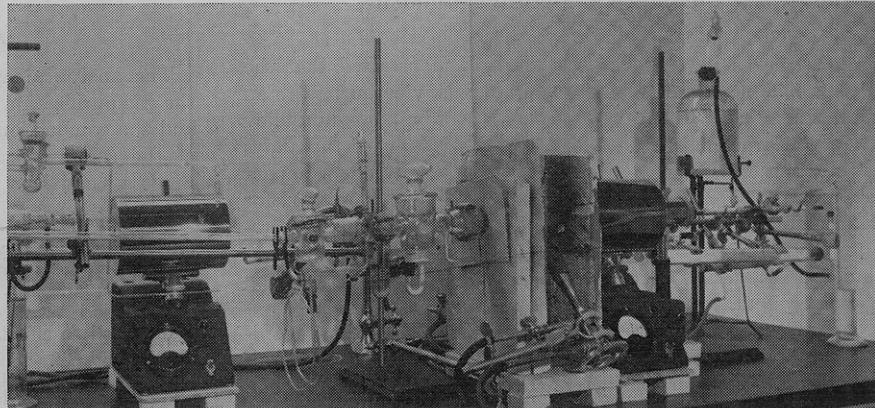


Figure 2. Over-all view of combustion train

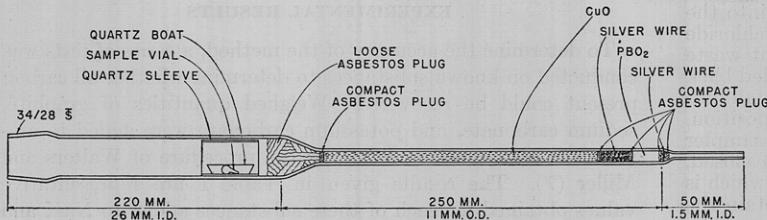


Figure 3. Quartz combustion tube

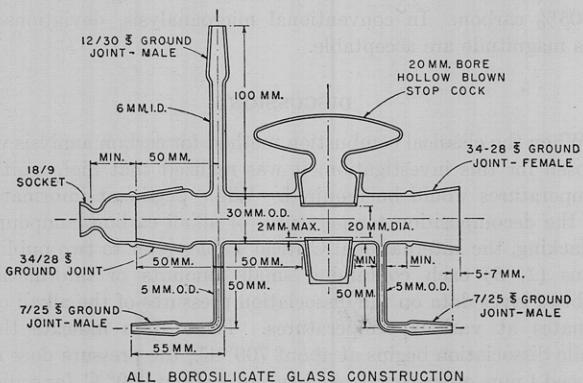


Figure 4. Introduction chamber

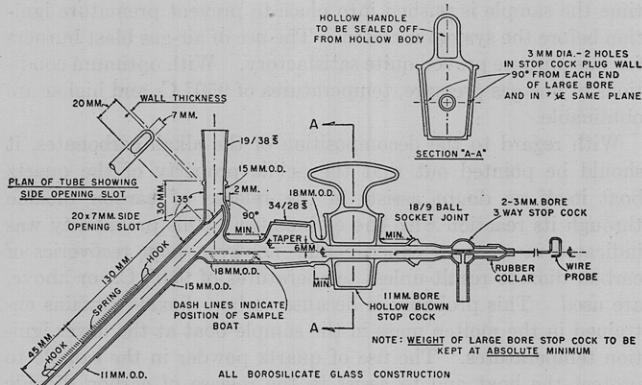


Figure 5. Sampling apparatus

SAMPLING FROM DYNAMIC SYSTEMS

Sampling NaK from a hot dynamic system requires a special technique and the use of specially designed equipment. To be analytically correct, the entire sample must be used for analysis; therefore it must be taken hot, for upon cooling of the sample segregation and precipitation of suspended and dissolved materials may occur. The apparatus described below makes it possible to take a sample that meets these requirements (Figure 5).

It consists of a large bore, hollow blown stopcock equipped on one side with a socket joint and on the other with a standard taper joint. This stopcock, which is lubricated with DC silicone grease, seals the sample from atmospheric contamination during handling, weighing, and transferring to the analytical apparatus. It is attached to a waste tube assembly which is designed to permit discarding waste or contaminated NaK from the sample valve prior to drawing the sample.

The sample valve (Figure 6) which must be an integral part of the system which is being sampled, is constructed without packing, and the fluid seal is accomplished by means of a steel bellows connecting the valve body to the valve stem. The design of the valve is such that manipulation of the valve subjects the bellows to only a spring action with no torsional effects. The

valve, as used, is an alteration of a standard valve (No. 1-314) manufactured by the Fulton Sylphon Co., Knoxville, Tenn. The alterations consisted of (a) reaming out the normal inlet and outlet connections to provide a straight through passage, (b) adding a threaded connection at the bottom, which contains the valve seat, to provide a means of connecting the sampling apparatus, and (c) extending the valve stem to reach the new valve seat location.

A metal (Invar) 19/38 joint (Figure 6) provides a tight connection between the sample valve and the sampling apparatus. A removable, thin-walled, stainless steel delivery tube seats against the open valve seat in such a manner as to direct the sample to the waste tube and sample boat from the sample line.

SAMPLING PROCEDURE

Before taking a sample, the sampler stopcock and a clean ignited sample boat are weighed to the nearest milligram. The apparatus (Figure 7) is assembled at the sampling site and pre-purified grade cylinder nitrogen is introduced through the 3-way stopcock to purge all the air from the system. Nitrogen flow is maintained throughout the sampling procedure at a rate of 5 to 7 liters per minute. The nitrogen velocity is more than sufficient to prevent significant counter diffusion of air into the apparatus.

When the apparatus has been purged for 3 to 5 minutes with the sample boat in position under the delivery tube and the waste tube in place above it, the sample valve is carefully opened to permit NaK to drop into the waste tube. Waste NaK, drawn

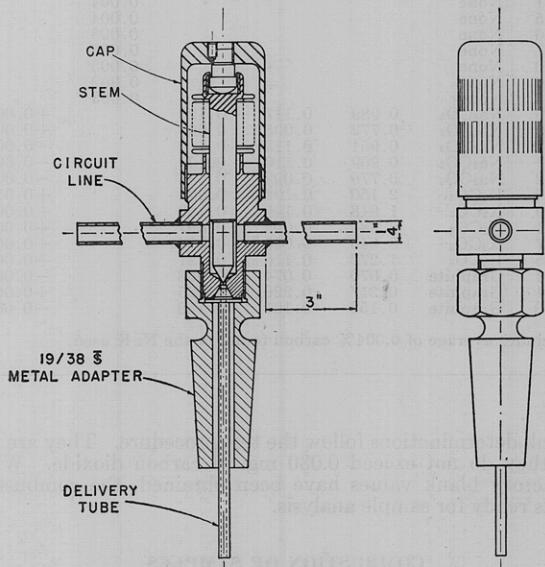


Figure 6. Sample valve assembly

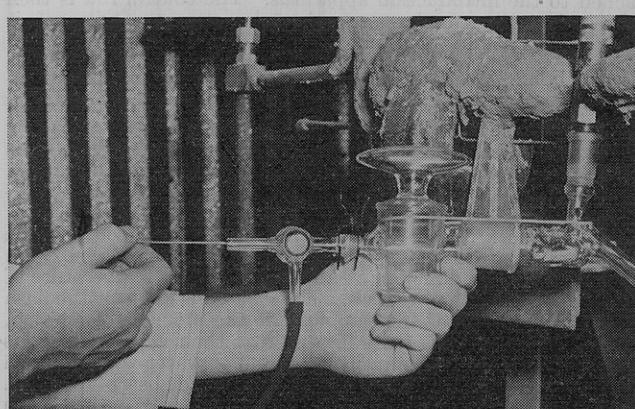


Figure 7. Sampling site

off to cleanse the valve seat of any static alloy, drops into the waste tube and from there into a scoop of potassium chloride crystals and is subsequently discarded. When sufficient waste NaK has been withdrawn, the waste tube is quickly pulled back to permit 2 drops (approximately 100 mg.) of sample to fall into the boat. The waste tube is then returned to its original position, the sample valve is closed, and the boat is pulled into the sampler stopcock, using the wire probe. The stopcock is then closed, sealing the sample within the bore of the stopcock plug which is then removed from the apparatus and reweighed to obtain the sample weight by difference.

TEST PROCEDURE

The train is assembled as shown in Figure 1, with the proper tube fillings as described above. Stopcock C is lubricated with silicone grease by applying it in strips 1 cm. in width at the top and bottom of the ground surface.

The standard taper on the combustion tube is twisted firmly into its mate on the introduction apparatus and then held together with steel springs. The rates of flow of the oxygen and of the air used for purging the absorption tubes after combustion of the sample are adjusted to 20 ml. per minute. All furnace temperatures are maintained on a 24-hour basis so that equilibrium conditions will not vary in the different tube fillings.

Table I. Recovery of Carbon Added to NaK Alloy

NaK, Mg.	Additive	Total C Mg. ^a	C Present, Mg. ^a	C Found, Mg.	C Found, % Mg.	Deviation, Mg.
103.0	None			0.005		
92.1	None			0.004		
157.5	None			0.004		
98.6	None			0.006		
98.7	None			0.003		
500.0	None			0.005		
600.0	None			0.002		
595.6	None			0.003		
96.0	Na ₂ CO ₃	0.989	0.117	0.123	+0.006	
132.3	Na ₂ CO ₃	0.772	0.095	0.099	+0.004	
147.7	Na ₂ CO ₃	0.951	0.113	0.110	-0.003	
121.7	Na ₂ CO ₃	0.969	0.116	0.109	-0.007	
91.2	Na ₂ CO ₃	0.770	0.092	0.086	-0.006	
100.5	K ₂ CO ₃	2.150	0.192	0.203	+0.011	
116.9	K ₂ CO ₃	1.618	0.149	0.153	+0.004	
108.1	K ₂ CO ₃	0.983	0.092	0.097	+0.005	
131.7	K ₂ CO ₃	0.640	0.063	0.069	+0.006	
103.5	K ₂ CO ₃	1.272	0.116	0.121	+0.005	
105.1	Graphite	0.070	0.074	0.068	-0.006	
67.1	Graphite	0.217	0.220	0.225	+0.005	
140.0	Graphite	0.155	0.161	0.158	-0.003	

^a Includes average of 0.004% carbon found in the NaK used.

Blank determinations follow the test procedure. They are run until they do not exceed 0.030 mg. of carbon dioxide. When satisfactory blank values have been obtained, the combustion train is ready for sample analysis.

COMBUSTION OF SAMPLES

After attaching weighed absorption tubes to the combustion tubes, the sampler stopcock holding the weighed sample is attached to the introduction apparatus. The control rod is then attached to the sampler stopcock and a stream of nitrogen is passed into the introduction chamber to flush all air and carbon dioxide from the entire introduction apparatus, from either side of the sampler stopcock, and from the push-pull rod housing. The sampler stopcock is then opened and the sample boat is pushed into the introduction chamber with the control rod, using a magnet. The large stopcock on the introduction chamber is then opened and the sample is pushed into the quartz sleeve in the combustion chamber. The control rod is then quickly withdrawn and the large stopcock is closed.

The stopcock on the Mariotte flask is then opened and the blast burners are lit. Care must be exercised to maintain oxygen flow in a positive direction at all times. As the temperature of the combustion chamber rises, a close watch is kept for the flash indicating ignition of the sample. At the moment of ignition, the oxygen demand is quite high so that the rate at which it is supplied must be momentarily increased or water will be drawn from the Mariotte flask into the safety tube and absorption tubes.

Completion of the combustion cycle and weighing of the carbon dioxide absorption tube follow closely that of conventional micro-combustion analyses.

EXPERIMENTAL RESULTS

To determine the accuracy of the method, a series of tests was conducted on known substances to determine whether all carbon present could be recovered. Weighed quantities of graphite, sodium carbonate, and potassium carbonate were added to ampules of NaK made up following the procedure of Walters and Miller (?). The results given in Table I are representative values obtained for each of these substances added to NaK and analyzed as mentioned above.

Results on the above recovery experiments vary from the theoretical amount of carbon added by an average deviation of 0.005% carbon. In conventional microanalysis, deviations of this magnitude are acceptable.

DISCUSSION

When the classical combustion method for carbon analysis was chosen for this investigation, it was realized that high ignition temperatures would be required. While pertinent information on the decomposition temperatures of alkali carbon compounds is lacking, the International Critical Tables refer to two publications (1, 3) each containing small amounts of information. Lebeau gives data on the dissociation pressures of the alkali carbonates at various temperatures. These data indicate that, while dissociation begins at about 700° C., the pressure does not exceed 1 mm. of pressure (mercury) until about 950° C. for sodium carbonate and 1000° C. for potassium carbonate. To obtain this temperature in the manner desired presents a problem, because the combustion chamber must be relatively cool at the time the sample is pushed into place to prevent premature ignition before the system is closed. The use of air-gas blast burners for this purpose proved quite satisfactory. With optimum conditions of line gas pressure, temperatures of 950° C. and higher are obtainable.

With regard to the decomposition of the alkali carbonates, it should be pointed out that the acidic property of the quartz boat itself no doubt assists in the release of carbon dioxide through its reaction with the carbonates. This probability was indicated in recovery experiments; however, poor recoveries of carbon dioxide result unless temperatures of 950° C. or above, are used. This probably is because carbon dioxide remains entrained in the molten mass in the sample boat at the lower ignition temperatures. The use of quartz powder in the sample to protect the boat and to assist in the release of carbon dioxide was foregone because of the high blank difficulties which seemed to result from its use.

Due to the protection afforded by the quartz sleeves which must be replaced after every 10 to 15 analyses, combustion tube mortality is low. One tube lasted for more than 150 analyses burning an average of 100 mg. of NaK each sample. Eventually, however, the fluxing action of hot alkali, and the repeated heating and cooling embrittle the quartz which then becomes porous—a condition which becomes evident by observing blank values.

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