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THE EFFECTS OF TRACE IMPURITIES OF MOISTURE, OXYGEN, HYDROGEN, NITROGEN AND CARBON DIOXIDE IN GLOVE BOX ATMOSPHERES ON THE ANALYSIS OF THE ALKALI METALS

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ABSTRACT

A survey was conducted at the request of the Atomic Energy Commission to examine the effects of atmospheric impurities during the handling of the alkali metals. Discussed in this report are: reactions between these impurities and the alkali metals, the effects of the impurities on some analytical procedures, and various dry box techniques for the handling of the alkali metals. Also included are suggested maximum permissible levels for these impurities as well as a bibliography of pertinent publications.

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PREFACE

This report is an evaluation of a literature survey that was undertaken at the request of the Division of Reactor Development and Technology, USAEC, to ascertain the effect of atmospheric contamination during sample handling on the analysis of alkali metals. Information was solicited from those chemists and metallurgists who are actively engaged in alkali metal analysis. While no attempt was made to associate any of the comments in this report with any particular individual or with any of the literary references which appear as a bibliography in the Appendix, all conclusions are based on the experiences of the author as well as on the comments of those of the individuals surveyed or on those references appearing in the literature. We wish to express our appreciation to the following individuals who cooperated so willingly either by supplying information based on personal experiences or by suggesting references in the open literature.

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INTRODUCTION

There is at present an increasing interest in the determination of impurities in the alkali metals in the order of 10 ppm or less. This interest has raised the question of the influence of atmospheric impurities, within the dry box in which the samples are handled, on the reliability of the analytical methods for the determination of these impurities. The impurities most likely to be present, and which would have an influence on the analytical results, are moisture, oxygen, hydrogen, nitrogen and carbon dioxide. We must therefore establish maximum permissible concentration levels for these impurities in order to increase the reliability of the analytical methods.

In order to fully explore the problem of the effects of these impurities on the analytical methods so as to establish maximum permissible concentration levels for these impurities, several factors were considered. We took into consideration the conditions which control the rates of reaction between the alkali metals and the impurities as well as the types of environmental systems that are presently in use for the handling of the metals. We also examined the analytical techniques which are used for the determination of these impurities and checked on the ability to detect and reduce the concentration of the impurities. This was done through a comprehensive study of readily available literature as well as direct contact with individuals actively engaged in working with the alkali metals.

IMPURITIES

Moisture

The presence of moisture as a contaminant in dry box atmospheres has the most serious effect of the impurities on the handling of alkali metals. Not only will moisture react rapidly with the alkali metals at low concentrations, but it will also enhance the reactions of the other impurities with the alkali metals. There is apparently little or no reaction between the alkali metals and the other impurities under consideration until well above the melting points of the metals. However,

as little as 10 to 15 ppm of moisture will cause the alkali metals to react with other of the impurities, such as oxygen and carbon dioxide, at room temperature. It has been suggested that this increased reaction rate is due in part to the hydrogen which is liberated when the moisture reacts with the alkali metal.

Oxygen

The factors which influence the reaction of the alkali metals with oxygen are somewhat involved. In the absence of moisture at room temperature, highly protective, thin film oxide coatings will form on the alkali metals. There is little or no reaction after this initial oxygen uptake. As the melting points are approached, the cracking of this oxide film will cause further reaction between the dry oxygen and the exposed metal. This reaction rate increases with an increase in temperature. The rate of reaction increases also with the increase in molecular weight of the alkali metal. The presence of hydrogen at as low a pressure as 0.005 mm caused sodium to react with dry oxygen at 270°C while no reaction was apparent even at 550°C in the absence of the hydrogen. It has also been shown that a few ppm of nitrogen will sensitize the surface of sodium metal and cause an increased reaction with dry oxygen. Other contaminants may well have a similar effect on the reaction of the alkali metals with dry oxygen. Lithium of 99.99% purity remained bright in air for up to 10 hours, while lithium of 99.9% purity blackened in seconds.

Hydrogen

The reaction between hydrogen and the alkali metals is negligible at room temperature. Its reaction with either lithium, sodium or potassium is not discernible until their respective melting points are reached, while the reaction with both rubidium and cesium is suppressed until a temperature of almost 600°C. The presence of any of the other contaminants has no effect on the reaction of hydrogen with the alkali metals.

Nitrogen

When neither argon nor helium are available, nitrogen may be used as an inert atmosphere within dry box systems when lithium is not involved. Lithium will react with nitrogen at room temperature to form a very thin, protective coating of nitride in the absence of moisture. Both the rate and extent of this reaction will increase rapidly at elevated temperatures or in the presence of either a small amount of oxygen or as little as

10 ppm of moisture. We have reported on the reaction of sodium with oxygen in the presence of nitrogen. For all practical purposes there is no reaction between nitrogen and the other alkali metals even at somewhat elevated temperatures or in the presence of other of the contaminants.

Carbon Dioxide

Dry carbon dioxide will react with lithium, sodium and potassium at temperatures in the order of 300°C and above and with rubidium and cesium at somewhat lower temperatures. At room temperature the reaction with the alkali metals is dependent on the presence of moisture to first form the alkali metal hydroxide which will in turn react with the carbon dioxide. Under certain conditions, carbon monoxide will react with the alkali metals at elevated temperatures to form carbonyls.

ENVIRONMENTAL SYSTEMS

At present, four types of environmental systems are in common use for the handling of the alkali metals. These are: a remotely operated high-vacuum box; a high vacuum-inert atmosphere glove box; a vacuum-inert atmosphere glove box in which the inert gas is continuously recycled during operation through a purification apparatus, and an inert atmosphere box equipped with both an evacuable transfer chamber and a gas recycling and purification system. The remotely operated box is always under vacuum and the containment systems to be sampled are introduced into the box through an evacuable transfer chamber. The sample is transferred from the container to a reaction vessel by either extrusion or melting. Encapsulation of samples within the box is accomplished by electron beam welding.

The high vacuum-inert atmosphere box is normally under vacuum when not in use. The purified, inert gas is admitted to the box just prior to use, and manipulation within the box is accomplished through rubber gloves. An evacuable transfer chamber is also a part of this box. Welding within this type of box is done by either helium or argon arc, depending on the inert gas used in conjunction with the box.

The recycling gas systems are becoming more and more popular. The inert gas is continuously recycled through a commercial unit which normally removes oxygen, moisture, hydrogen and carbon dioxide to parts-per-million quantities. Again, the vacuum-inert atmosphere glove box is under vacuum when not in use. The purification apparatus is operated

only when the box contains an inert atmosphere. The inert atmosphere box with an evacuable transfer chamber is partially evacuated and then flushed with the inert gas for several such cycles. The box is then maintained under an inert atmosphere of the continuously recycling gas for extended periods of time whether or not the box is in actual use.

DISCUSSION

With the exception of the remotely operated extrusion sampler and the vacuum amalgamation technique for the determination of oxygen used at Lewis-NASA, the distillation method, and certain in-line instrumentation techniques, other analytical methods for the determination of contaminants in the alkali metals are at one time or another subject to exposure to an inert atmosphere. The more routine methods involve the determination of oxygen, carbon and hydrogen. In each case the sample first must be transferred to a suitable reaction apparatus. The analysis is usually carried out under an inert atmosphere either within or outside of the dry box in which the sample was transferred to the reaction vessel. Both helium and argon are acceptable cover gases with helium being preferable in systems which incorporate liquid nitrogen cold traps.

Fortunately, modern instrumentation and technology affords us the ability to detect and remove microgram amounts of the contaminants just discussed from the high purity systems under consideration. There are many commercially available trace oxygen analyzers, hygrometers and gas chromatographs. These instruments are capable of detecting as little as 1 ppm of these contaminants. Several commercial gas purification and recycling apparati are also available which are capable of reducing the concentration of these contaminants to less than 1 ppm. In addition, we can resort to hot titanium, uranium or zirconium getter traps, as well as molecular sieve and cold traps, to reduce the concentration of the contaminants in the inert gas prior to the introduction of this gas into the high purity system.

The problems are different for the high-vacuum, remotely operated dry boxes and the vacuum analytical systems. It has been found that a vacuum of at least 1×10^{-5} torr is necessary for reproducible analytical results. However, it is possible to use a vacuum system which is capable of only 10^{-3} torr if the system is flushed several times with an inert

gas of high purity. Conversely, a system capable of operating at 10^{-8} torr which is pumping at 10^{-5} torr subjects the sample to a continuous leak and contamination while theoretically operating at a pressure void of contamination. Fortunately, leak-tight, high vacuum systems are no longer difficult to obtain at relatively low costs.

RECOMMENDATIONS AND CONCLUSIONS

The following values, recommended for the maximum concentration levels of the impurities, are based on normal dry box operations and minimum exposure time of the alkali metal sample during transfer of the sample to the reaction system: moisture, less than 5 ppm; oxygen, less than 10 ppm; hydrogen, less than 5 ppm; nitrogen, less than 10 ppm (in the handling of lithium); and carbon dioxide, less than 10 ppm. Exceptions can be made. If, for example, one were analyzing for carbon, larger concentrations of oxygen, hydrogen or even moisture could be tolerated in the absence of carbon dioxide. One should also realize that a sample transferred into a small reaction vessel for subsequent analysis for oxygen by the amalgamation procedure is exposed to far less of the contaminant than a sample which is amalgamated within the dry box. Also, solid, cold samples are less likely to react with the contaminants than molten samples.

Although we have mentioned various techniques by which the concentrations of these contaminants can easily be reduced to well below the desired levels, there are problems attendant to maintaining these low levels. We have already discussed the possibility of contamination in the high-vacuum systems. Returning to the high-purity inert gas systems, we find that aside from leaks in the box or the vacuum system, which can be readily corrected, the main source of contamination is the rubber gloves used to manipulate the sample within the box. Tests with neoprene and butyl rubber gloves show that while the increase of oxygen, hydrogen, nitrogen and carbon dioxide through diffusion is negligible, the diffusion of moisture is a matter for concern.

The butyl rubber gloves appear to be preferable to the other types of available gloves. However, these same gloves have been found to add 0.01 g. of water vapor per hour to a dry box when exposed to average temperature and humidity. This value increases tenfold when the gloves are in use. The permeation rate is dependent on both the partial

pressure differential of the water vapor across the glove and the thickness of the glove. Neoprene gloves have been known to add moisture at the rate of 50 ppm per hour. Gloves made of polymers with halogens have the additional disadvantage of reacting with the more active alkali metals, especially cesium. At present the only known solution to the glove problem is the use of a second pair of gloves within the glove attached to the dry box. Of further value is the flow of a continuous stream of dry air or inert gas between the two pairs of gloves.

At first glance it would appear that for general use the dry box which incorporates the recycling purification system is the panacea for all our problems. With the exception of water vapor contamination, this might well be the case. While it is true that the purification unit will remove the moisture as well as the other contaminants from the dry box atmosphere to well below the suggested maximum levels, we must remember that additional water vapor is continuously diffusing through the gloves into the box, and, of necessity, in close proximity to the samples being handled through the use of the gloves. However, this type of dry box can be used for an hour or more before one notes discoloration of the alkali metal due to contamination. While this type of box need not be evacuated between samplings, the glove ports should be sealed and kept under vacuum when the box is not in use. This type of sample handling system does, however, have a definite advantage over the regular vacuum-dry box which can be used for only a short period of time before discoloration is noted and which must be evacuated between samplings. The use of a second pair of gloves almost doubles the working time in both these systems before contamination is noted.

In making these recommendations it is by no means felt that our problems are solved. The continuous development of more precise methods may eventually warrant a need for even lower levels of contamination. At this time it would be impractical to suggest that we establish levels of less than 5 ppm when such a high degree of purity does not seem to be necessary. Nor is it recommended that everyone be made to incorporate a gas recycling purification unit into their dry box operation. We do believe that all alkali metals work should be restricted to high vacuum-high purity systems such as just discussed. It is further recommended that two pairs of gloves should be used during sample handling and that additional work should be done toward the development of a better dry

box glove. (What of a laminated glove with a moisture barrier sealed between two layers of rubber?) And finally, it would be beneficial to standardize the methods of sampling and analysis with consideration given to the equipment and funds that may be available to the average analytical facility.

APPENDIX

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