

SURVEY OF SIMPLE CARBON COMPOUNDS FOR USE IN A NEGATIVE ION
SPUTTER SOURCE

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ABSTRACT. We present a survey of carbon beam yields from 20 simple carbon compounds using a caesium sputter source and the McMaster University tandem accelerator. The carbon yield was measured as a 35MeV $^{12}\text{C}^{4+}$ beam. We found that the beam intensities could be related to a grouping of the carbides according to the chemical bonding of the compounds. The usefulness of the compounds for accelerator ^{14}C dating was further related to their preparation chemistries. Strontium carbide was the equal of graphite in negative carbon ion beam production and aluminum carbide was found to be a good candidate for further tests because of its good sputter yield and preparation chemistry. Charcoal was also tested with varying amounts of silver added as a heat conduction aid.

INTRODUCTION

The use of tandem electrostatic accelerators as sensitive mass spectrometers in studying radioisotopes has become well-established in recent years (Gove, 1978; Kutschera, 1981). This technique makes possible the ^{14}C dating of small samples which were heretofore difficult or impossible to date using decay counting techniques. The accelerator method requires only a few milligrams or less of carbon but the best chemical form of the carbon for use in these systems is still under investigation. A survey of simple carbon compounds with a range of properties and preparation chemistries was made to find suitable sample preparation methods.

The criteria that the sample preparation procedure must meet for accelerator dating are generally the same as those required for decay counting. In both methods, it is very difficult to determine accurately the absolute measurement efficiencies, and for the accelerator systems, the efficiency for one isotope relative to the other. The simplest solution is to measure all unknowns with respect to standards in a system with constant relative isotopic efficiencies. This

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requires a sample preparation technique in which all samples are treated and presented for measurement identically. The preparation chemistry must be quantitative at all stages to preclude isotopic fractionation which may vary from sample to sample. The final product must be a homogeneous substance that remains well-mixed isotopically throughout the measurement.

For routine use, the preparation must have a reasonable through-put and be capable of handling small samples without contamination. For accelerator dating, the resultant substance should produce a long-lived intense C⁻ beam with a short stabilization time in the ion source lest accelerator time be wasted.

Perhaps the simplest substance to fit these needs is CO₂, which is easily prepared in a quantitative homogeneous manner. However, attempts to use CO₂ directly for accelerator dating have not been successful because of source memory effects (Shea et al, 1980; Heinemeier and Andersen, 1983).

Most laboratories use Cs sputter ion sources that require the sample to be in solid form. Various solids can be derived from CO₂. The gas can be reduced and then cracked to graphite in a slow glow discharge process which is almost quantitative but the deposit of which is thin and quickly sputtered away (Grootes et al, 1980; 1981). Alternatively, acetylene can be produced from CO₂, as is done in benzene synthesis (Tamers, 1975). Graphite can be produced from acetylene by radio-frequency dissociation (Beukens and Lee, 1981) or thermal pyrolysis (Hedges, Wand, and White, 1980). However, these methods have low yields (~60%) and produce isotopically inhomogeneous samples (Elmore, 1981; Hedges, Wand, and White, 1980). The carbonates and carbides chosen for this study can also be made from one or the other of these two gases. Charcoal is included and graphite is the standard against which all are judged.

CARBIDES. Carbides can be classified into five groups based on their macroscopic properties (Hough, 1964) and their chemical bonding (Samsonov, 1965): 1) ionic or salt-like, 2) covalent or diamond-like, 3) metallic, 4) volatile, 5) graphites (fig 1). Both the ionic and metallic groups have subgroups. Gaseous volatile "carbides", and explosive ionic-metallic carbides were not considered, as they are incompatible with the sputter source. Graphites (Hennig, 1959) were also not investigated, as they are interstitial variations on graphite and would offer no benefits over true graphite in the preparation or sputtering phases. Sixteen metal carbides (plus graphite) were chosen for study to represent the remaining major types. All of the refractory transition metal

Fig 1. Periodic table of the binary carbides grouped according to the chemical bonding of the compound. Elements not included are those for which the existence of a binary carbide has not been demonstrated.

Frad (1968) wrote an extensive review of metal carbide properties and preparation. One general method of preparation is carburization, in which a metal or metal oxide is heated in the presence of fine carbon powder, acetylene black, or a hydrocarbon. This approach lends itself to miniaturization and can make use of the acetylene produced in benzene preparation. Vapor phase deposition (Campbell et al, 1949; Powell, 1966) is a well-documented technique in which a mixed vapor of hydrocarbon and the metal halide react, forming the metal carbide on a hot filament (tungsten or tantalum). The process is similar to thermal pyrolysis of hydrocarbons to graphite. However, unless deposition is much more efficient or less fractionating than pyrolysis, the latter would be preferred. The acetylides (the ionic and ionic-metallic carbides) can be produced by precipitation from a liquid ammonia solution of the metal by bubbling acetylene through it. The precipitate is primarily the metal hydro-acetylide (MeHC_2 or $\text{Me}(\text{HC}_2)_2$) with some ammonia and excess acetylene co-ordinated with metal ions. Gentle heating from the -30° liquid ammonia temperature will drive off the ammonia and convert the hydro-acetylide to a carbide of 98 to 99% purity (Corbellini and Turner, 1960). This method is easily used for small quantities, is stoichiometric, and yields a well-mixed carbide. Some carbon will be

lost as acetylene in the last heating phase, however. Other techniques of less general carbide production exist, eg, the direct production from lithium and carbon dioxide or the reduction of the carbonates of calcium, barium, and strontium to their respective carbides and oxides by heating with magnesium metal.

METHODS AND RESULTS

The caesium sputter source was of the Middleton type (Middleton and Adams, 1974) used in the reflected mode. Our measurements were made at the FN Tandem Van de Graaff accelerator at McMaster University where the carbon yields were measured as 35MeV $^{12}\text{C}^{4+}$ at the image Faraday cup of the analyzing magnet. Using the analyzed high-energy beam eliminates any background ions introduced by the low resolution inflection magnet.

All compounds were commercial >99% pure chemicals¹. Samples were prepared using the pure compound and using the compound mixed 1:1 with 100 mesh silver powder. Hedges, Wand, and White (1980) found that high sample temperatures impair sputtering of negative ions by evaporating caesium from the surface, whereas the addition of silver powder aids sputtering by increasing the thermal conductivity of the sample. The 1:1 ratio of silver to compound was used throughout for consistency, but much larger amounts of silver (up to 20 or more to 1) are more effective (Grootes *et al.*, 1981). Compounds that might react with water vapor in the air were capped with a layer of silver which was scraped away before loading into the source.

Each measurement followed a sequence: 1) checking the current from the graphite standard, 2) an initial current from the sample, 3) current readings 10 and 20 minutes later, and 4) checking the current from graphite. Most samples showed increasing currents in the first few minutes as the surface became caesiated, and most had stabilized before the 20-minute reading was taken. If the current was still increasing at that time, the sample was run for another 10 minutes and the continued increase noted. The source was operated at 25 kV extraction voltage producing 5 μAmps of mass 12 negative ions from graphite.

Table 1 shows the 35MeV $^{12}\text{C}^{4+}$ current obtained as a fraction of that of graphite after 20 minutes for each compound, plain and with silver added, averaged for 2 or 3 runs on separately prepared samples. Uncertainties of up to 25% were expected due to variations in sample packing, sample holder heat conduction, and ion source behavior.

¹Alfa Products, Danvers Massachusetts

TABLE 1. 35MeV $^{12}\text{C}^{4+}$ yields from sputtered carbon compounds measured relative to that of graphite

Compound	Relative yield	Relative yield with Ag added*	Compound	Relative yield	Relative yield with Ag added*
CARBIDES					
Ionic			Covalent		
CaC_2	0.19	0.48	B_4C	0.08	0.20
SrC_2	1.06	0.80	graphite	1.00	1.10
BaC_2	0.38	0.60	SiC	0.12	0.27
Ionic covalent			CARBONATES		
Al_4C_3	0.18	0.36	Na_2CO_3	0.01	
Metallic			K_2CO_3	0.01	
TiC	0.18	0.26	CaCO_3	0.01	
ZrC	0.15	0.10	CHARCOAL**		
HfC	0.15	0.14	No Ag	0.09	
VC	0.26	0.31	1:1 Ag	0.13	
NbC	0.23	0.20	1:2 Ag	0.11	
TaC	0.10	0.14	1:5 Ag	0.20	
Cr_3C_2	0.27	0.32	1:10 Ag	0.23	
Mo_2C	0.00	0.02			
WC	0.21	0.15			
Metallic-iron					
Fe_3C	0.03	0.03			

* silver was added in 1 to 1 ratio by weight

** ratio of added silver is by weight

TABLE 2. Carbide group average yields of $^{12}\text{C}^{4+}$ measured relative to yield of graphite

Group	Relative yield	Relative yield with Ag added
Ionic (3)*	0.54	0.63
Ionic-covalent (1)	0.18	0.36
Covalent (2)	0.10	0.24
Metallic (9)	0.17	0.18
Metallic-iron (1)	0.03	0.03

* number in parentheses is number of compounds in that group used in this study

DISCUSSION

CARBIDE SPUTTERING. Table 2 summarizes the relative sputtering yields of each carbide group. Ionic bonded compounds are more easily sputtered, with covalent and metallic compounds less so. The salt-like acetylides give over 50% the carbon current of graphite, with improvement upon addition of silver. In these compounds, the carbon clearly exists within the molecule as a negative ion attached to the positive metal ion. On several tests, pure strontium carbide was the equal (within uncertainties) of graphite. It is not clear why strontium was better than calcium or barium. Strontium carbide is produced by some laboratories as an intermediate step in acetylene and benzene production using the carbonate-magnesium process mentioned above. A sample of strontium carbide, strontium oxide, and magnesium oxide was prepared in the proportions of such a reaction. This sample, with or without silver, proved to be a poor negative carbon ion source. The strontium oxide inhibited the carbon sputtering, making an otherwise attractive production method unusable. The liquid ammonia method of preparation may still allow use of the alkali-earth carbides; however, the oxide inhibition means that the sample would have to be protected from water vapor in the air. The expensive group III and rare earth metals were not considered viable for routine use. The alkali carbides are less attractive in that, except for lithium, they tend to form compounds other than the simple carbide (Samsonov, 1965).

Magnesium, beryllium, and aluminum form carbides in which some covalent bonding of the metal ions is important. Magnesium carbide was not available, but can be made through carburization of the metal by acetylene. The difficulty in handling the powdered magnesium may preclude its use. Beryllium carbide exists as a single carbon anion attached to a covalently bound Be cation, has a high thermal conductivity and might be an excellent source of carbon ions. Health dangers of beryllium and its compounds, as well as the need to keep a low beryllium background in our source for Be dating purposes, preclude the use of this compound. Aluminum carbide is a reasonably good carbon ion source and improves greatly when heat conducting metal is added. The stronger covalent contribution to the bonding in aluminum carbide reduces its yield but also makes it much more stable against decomposition (to methane). If it were produced by carburization, a large over-supply of aluminum powder would result in a well-mixed, heat-conductive sample.

Covalent carbides, excluding graphite, are not as efficient as ionic compounds. The addition of silver to boron

and silicon carbides increases their yields substantially, indicating that heat conduction is a limiting factor. (These carbides have heat conductivities 5 and 10 times smaller than graphite (Hough, 1964)).

The transition metal (refractory) carbides are commercially important and have well-studied properties (Samsonov and Vinitskii, 1980). They are all interstitial in character wherein a lattice of metal atoms accepts carbon atoms into certain positions, resulting in the formation of MeC_f where f has 1.0 as its upper limit. Except for vanadium and chromium, the sputter yields from the metal carbides are mediocre. Their heat conductivities are generally low ($0.01 - 0.07 \text{ cal/cm} \cdot \text{sec}^\circ\text{C}$) and the addition of 1:1 silver produced little improvement. One run made on samples scrupulously similar in preparation indicated that the C- yield was related to the heat of atomization for these carbides. Vasil'yev (1980) shows a similar dependence in the sputtering yield of positive metal ions from these compounds. Vapor deposition is the standard way to make small quantities of the refractories and little appears to be gained from making these carbides instead of pyrolyzed graphite.

The iron metallic carbides differ from the transition metallic carbides principally in having less simple crystal lattices with vacancies for carbon. These metals do not form mono-carbides and the increased bonds may contribute to the low sputter yields, although chromium carbide, which is in a transition position between the two metallic groups, is a good sputterer. Several authors report widely differing carbon beams from cast iron and carbon-iron mixtures (Ball *et al.*, 1981; Leavitt, Donahue, and Long, 1981; Grootes *et al.*, 1981; Middleton, 1978). However, it is not clear in these cases how much, if any, of the carbon is in the form of iron carbide.

CARBONATES. The carbonates of sodium, potassium, and calcium were tested as representatives of the alkali and alkali-earth carbonates. These compounds are of interest because they are easily made by precipitation from CO_2 . Unfortunately, the carbon sputter yields were only 1% of graphite, too low to be useful.

CHARCOAL. Charcoal as a carbon ion source is simply prepared: the sample is cleaned and then charred in an oven. However, not all samples and standards can be prepared in this way, and problems in comparisons are introduced. Table 1 indicates that at least 5:1 or 10:1 silver must be added to charcoal to get a respectable sputter yield. The grains in even hard-packed charcoal give poor thermal conduction. Grootes *et al.* (1981) report almost 50% the beam from graphite by using 8:1 and 16:1 mixes of silver and charcoal.

CONCLUSION

From our survey of the sputtering yields of carbon from the various types of simple carbon compounds, we found that ionic and ionic-covalent carbides produce carbon beams that are a large fraction of those from graphite. Two carbides, SrC_2 and Al_4C_3 , merit further investigation in order to make production techniques for small samples routinely quantitative. Aluminum carbide, in particular, offers a good beam, reasonable stability in handling, and an obvious production technique making use of acetylene from an already established sample preparation system. We have further seen that the negative ion sputtering yield from carbides depends primarily on bonding and thermal conduction effects.

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