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Surface Composition Determined by Analysis of Impact Radiation

Surface constituents are determined by an analysis of radiation from low-energy particle-surface collisions.

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A novel and sensitive technique for the analysis of surface composition has been developed. Called SCANIIR (surface composition by analysis of neutral and ion impact radiation), this technique evolved from the recent discovery that visible, ultraviolet, and infrared radiation is produced when a beam of low-energy (30 electron volts and above) ions (*1*), or neutral atoms or neutral molecules (neutrals) (*2*), impact on a surface. The subject of this article is the application of the SCANIIR technique to the problem of the analysis of the surface composition of complex solids (volcanic glass and a tektite) and the analysis of the composition of microliter quantities of liquids containing both organic and inorganic material (for example, human blood). In addition, the radiation that is produced when various materials of known composition are bombarded with projectiles will be discussed. Finally, results obtained from the impact of a neutral species on a silicate melt containing known concentrations of impurities will be presented to give an indication of the sensitivity of the technique.

Our recent experiments have shown that the optical line radiation produced in the collisions of low-energy ions and neutrals with surfaces arises from the decay of excited states of the atoms and molecules that are characteristic of the surface constituents, including surface contaminants. The interaction of the impinging projectile beam with the surface results in the ejection of neutral atoms, neutral molecules, and ions from the surface through a process known as sputtering (*3*, p. 142). A significant portion of the sputtered fragments leave the surface in excited electronic states and subsequently give rise to the observed optical radiation. One can determine the surface constituents by analyzing the spectral distribution of radiation and identifying prominent optical lines and bands. The intensities of the individual spectral lines are proportional to the absolute concentrations of specific surface constituents within the penetration depth of the incident projectile.

The SCANIIR technique is largely nondestructive because low bombarding energies (less than 4 kiloelectron volts) are used. During the time interval (approximately 30 minutes) required to obtain a complete spectral scan, however, several monolayers of surface material are removed by the impinging beam. The use of low bombarding energies results in a very sensitive probe of the surface region because the range of the incident projectile in the solid is limited to at most a few monolayers. Detection capabilities range from 1 part in 10^6 to a few parts in 10^4 under present operating conditions.

Experimental Apparatus

The apparatus used in this work (see Fig. 1) is capable of producing beams of ions or neutrals of well-defined energy in the range from 10 electron volts to 4 kiloelectron volts. In general, we find neutral atoms and molecules to be more useful projectiles than ions since problems associated with charge accumulation on nonconducting surfaces are avoided. In either case, the first step is the creation of ions in the source region by means of electron bombardment of either nitrogen molecules or one of the rare gases. Ions are then withdrawn from the source region, accelerated to the desired energy, and focused into a charge-exchange chamber where fast neutrals can be created from the ions by means of resonant charge transfer. This process involves little momentum transfer, and consequently the resulting neutrals have essentially the same energy and direction as the initial ions (*4*). In general, the gas pressure in the charge-exchange chamber is adjusted to produce approximately 30 percent neutralization of the incident ion beam. After passage through the charge-exchange chamber the remaining ions can be deflected out of the beam, leaving only neutrals to enter the target chamber. The solid to be bombarded is oriented in the target chamber with the surface normal at an angle of approximately 45° to 60° with respect to the direction of the incident beam. The target chamber is equipped with a quartz window for viewing the interaction region, and photons, which are produced as a result of the collisions of the neutrals with the surface, are focused by a quartz lens into an *f*/5, 0.3-meter monochromator. The monochromator and a cooled photomultiplier are used to record the spectral distribution of radiation produced in the collision process. Single photon counting techniques are used to enhance the sensitivity of the system for the detection of radiation. The neutral beam flux in the target chamber is measured by a bolometer which also can be operated as a Faraday cup to

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measure ion current (*5*). The neutral beam intensity varies as a function of beam energy from 1×10^{-8} ampere (equivalent neutral current) at 30 electron volts to 1×10^{-6} ampere at 4 kiloelectron volts. The beam diameter ranges from 2 to 3 millimeters.

The aperture separating the intermediate chamber (the charge-exchange chamber is contained in the intermediate chamber) and the target chamber is 3 millimeters in diameter. Each chamber is evacuated with a mercury diffusion pump having a liquid nitrogen trap in order to minimize excessive hydrocarbon contamination which might possibly be incurred if oil diffusion pumps were used. A pressure of 3×10^{-7} torr is achieved in the target chamber with a gas pressure of 10^{-3} torr in the source and charge-exchange chambers.

Radiation from Known Materials

In all cases, the optical radiation produced as a result of the impact of low-energy neutrals on solid surfaces consists of lines and bands that are characteristic of the surface constituents, including surface contaminants. Examples of the spectral distribution of radiation produced by the impact of nitrogen molecules (N_2^0) (beam energy of 3.5 kiloelectron volts) on aluminum oxide (Al_2O_3), lithium fluoride (LiF), and quartz (SiO_2) are shown in Fig. 2. In each case, the equivalent neutral current was approximately 3×10^{-7} ampere. Similar results were obtained with the use of neutral argon or neon atoms at the same energy. The prominent optical lines in the scans shown in Fig. 2 have been identified as arising from the decay of excited states of neutral aluminum, lithium, silicon, and hydrogen. The widths of all of these lines are limited by the slit settings (5-angstrom resolution in Fig. 2), but in higher resolution scans over selected wavelength intervals they are observed to be less than 1 angstrom in width. On the basis of this finding we conclude that the radiation arises from atoms and molecules which have been sputtered off the surface in excited states and are radiating as essentially free atoms and molecules (*6*). Balmer lines of neutral hydrogen, which are observed in the impact of N_2^0 on quartz, result from the interaction of the impinging beam with residual surface contaminants (water vapor or hydrocarbons). In contrast to the radiation from sputtered silicon atoms, hydrogen radiation decreases when the sample is heated to drive off surface contaminants.

Excited states of fluorine and oxygen, which would give rise to radiation in the wavelength interval from 1900 to 8400 angstroms, either are not populated in the collision or are de-excited by nonradiative processes. However, the resonance lines of these atoms, which we expect to be the most intense, lie in the vacuum ultraviolet, an optical region in which measurements thus far have not been made.

The same optical emission lines shown in Fig. 2 are produced if the ions N_2^+, Ar^+, or Ne^+ are used as incident projectiles, but in these cases positive charge accumulates on the nonconducting surfaces; this charge buildup decreases the energy of the impinging ions and causes defocusing of the ion beam (*7*). However, if a conducting target is used, neutrals and ions (of the same species) are found to produce photons with equal efficiency. Ions at low energies impinging on a metallic target are neutralized by nonradiative processes several angstroms in front of the surface (*3*, p. 241; *8*), before the close-in sputtering encounter occurs. Photons result from the sputtering encounter, and thus the photon production efficiency from a metallic target should be the same for both ions and neutrals at the same energy; this prediction has been confirmed by experiment. This result can be used as a means for the measurement of the neutral beam flux in the low-energy region. The ratio of the intensity of the optical line radiation produced when a metallic target is bombarded with neutrals to that produced when a metallic target is bombarded with ions is equal to the ratio of the neutral "current" to the easily measured ion current.

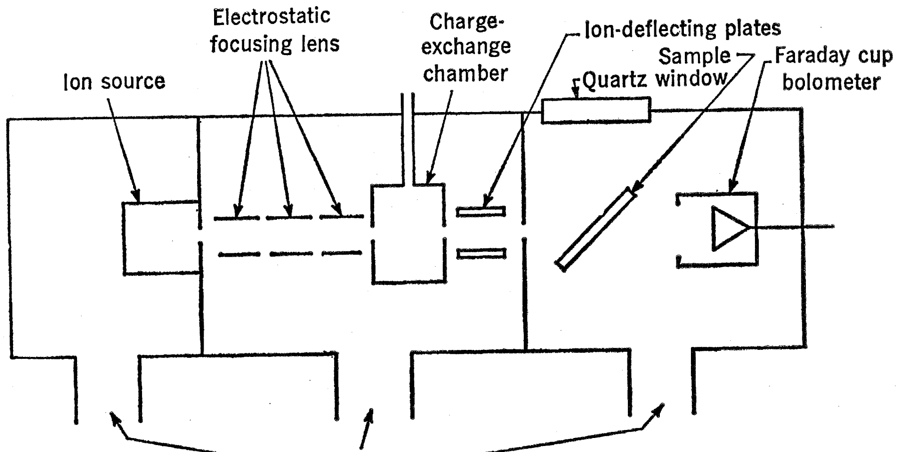


Fig. 1. Schematic diagram of the neutral beam apparatus.

Radiation from Complex Samples

We have applied the technique of observing and analyzing collision-induced radiation to a number of complex unknown solids. As examples of this type of application we discuss results obtained from the use of samples of volcanic glass and a textite. Both of these petrological samples were washed in xylene, acetone, and deionized water prior to insertion into the apparatus to remove dust and other contaminants.

The spectral distribution of radiation produced by the impact of N_2^0 (energy of 3.5 kiloelectron volts) on the surface of the volcanic glass and the tektite is shown in Fig. 3. These spectral scans were acquired in a time period of 30 minutes each, and in each case an equivalent neutral beam current of 3×10^{-7} ampere was used. It is possible to assign the prominent optical lines to specific elements by comparing the spectrum from the unknown with previously determined spectra characteristic of pure materials. Radiation from common elements such as silicon, aluminum, sodium, and calcium is evident in both scans. The tektite contains, in addition, iron and magnesium. There are a number of lines in both scans which have not as yet been assigned to specific elements.

Radiation from Human Blood

The SCANIIR technique also has been applied to the qualitative analysis of the composition of very small quantities of liquid residues containing both organic and inorganic material. The experimental procedure we use is to deposit the liquid on a clean quartz substrate and allow the water to evaporate. Neutral argon or nitrogen is used to bombard the substrate, and the collision-induced spectrum of radiation is recorded and analyzed.

To demonstrate the application of this technique to liquid residues, human blood was used as the "unknown" sample. Blood is routinely analyzed in many clinical laboratories by a variety of techniques, most of which require a reasonably large sample volume (approximately 1 cubic centimeter or more). In many cases, however, the sample volume that can be safely taken from a patient is significantly less than this, as is the case for premature infants and very small children. These increasingly smaller sample volumes re-

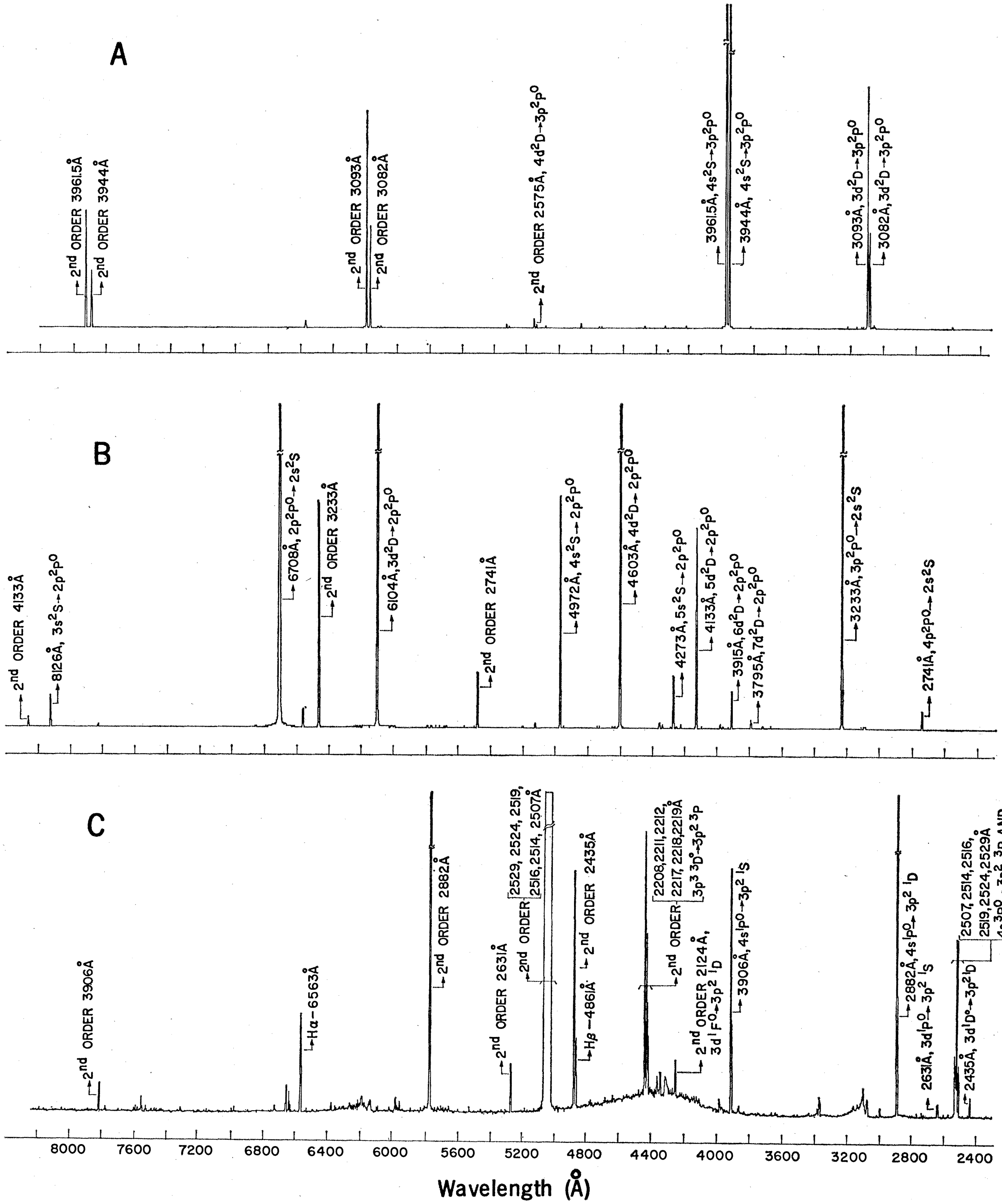
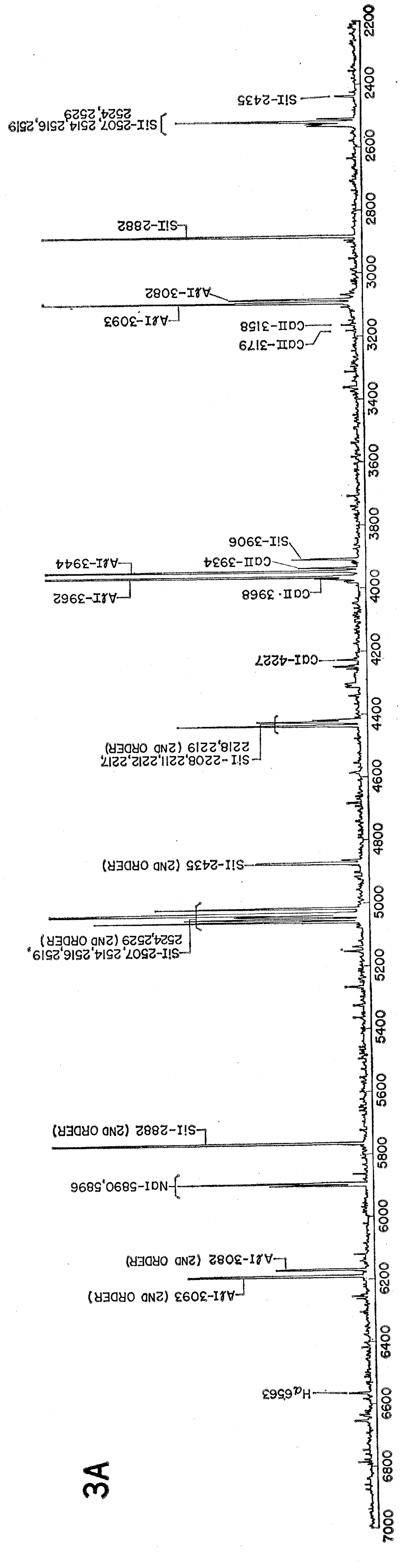


Fig. 2. Spectrum of radiation produced by the impact of N_2^0 (3.5 kiloelectron volts) on (A) Al_2O_3, (B) LiF, and (C) SiO_2. Lines arising from excited states of neutral aluminum, lithium, and silicon are observed in this wavelength interval. The wavelength and electronic transition are indicated beside each line. Two Balmer lines of neutral hydrogen, H_α and H_β, are also observed on the SiO_2 scan.

3A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SiI-2435
SiI-2882
AlI-3082
AlI-3093
CaII-3158
CaII-3179
SiI-3906
CaII-3934
AlI-3944
AlI-3962
CaII-3968
CaI-4227
SiI-2208,2211,2212,2217, 2218,2219 (2ND ORDER)
SiI-2435 (2ND ORDER)
SiI-2507,2514,2516,2519, 2524,2529 (2ND ORDER)
SiI-2882 (2ND ORDER)
NaI-5890,5896
AlI-3082 (2ND ORDER)
AlI-3093 (2ND ORDER)
Hα6563
2200
2400
2600
2800
3000
3200
3400
3600
3800
4000
4200
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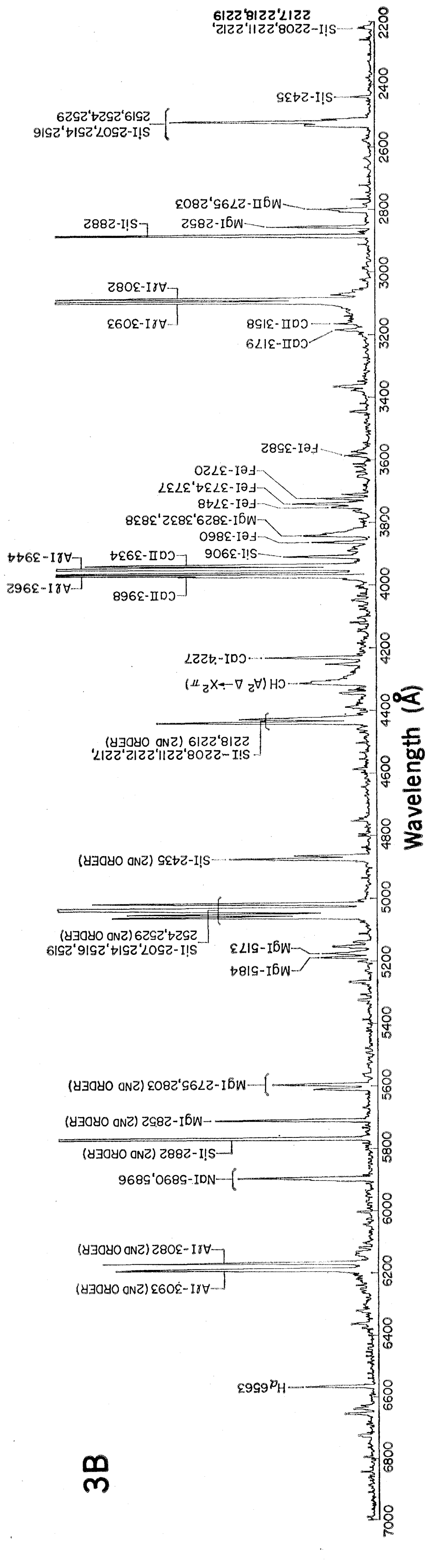
6800
7000

3B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SiI-2435
SiI-2507,2514,2516 2519,2524,2529
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MgI-2852
SiI-2882
AlI-3082
AlI-3093
CaII-3158
CaII-3179
FeI-3582
FeI-3720
FeI-3734,3737
FeI-3748
MgI-3829,3832,3838
FeI-3860
SiI-3906
CaII-3934
AlI-3944
AlI-3962
CaII-3968
CaI-4227
CH (A²Δ→X²π)
SiI-2208,2211,2212,2217, 2218,2219 (2ND ORDER)
SiI-2435 (2ND ORDER)
SiI-2507,2514,2516,2519 2524,2529 (2ND ORDER)
MgI-5173
MgI-5184
MgI-2795,2803 (2ND ORDER)
MgI-2852 (2ND ORDER)
SiI-2882 (2ND ORDER)
NaI-5890,5896
AlI-3082 (2ND ORDER)
AlI-3093 (2ND ORDER)
Hα6563
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2600
2800
3000
3200
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3600
3800
4000
4200
4400
4600
4800
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5200
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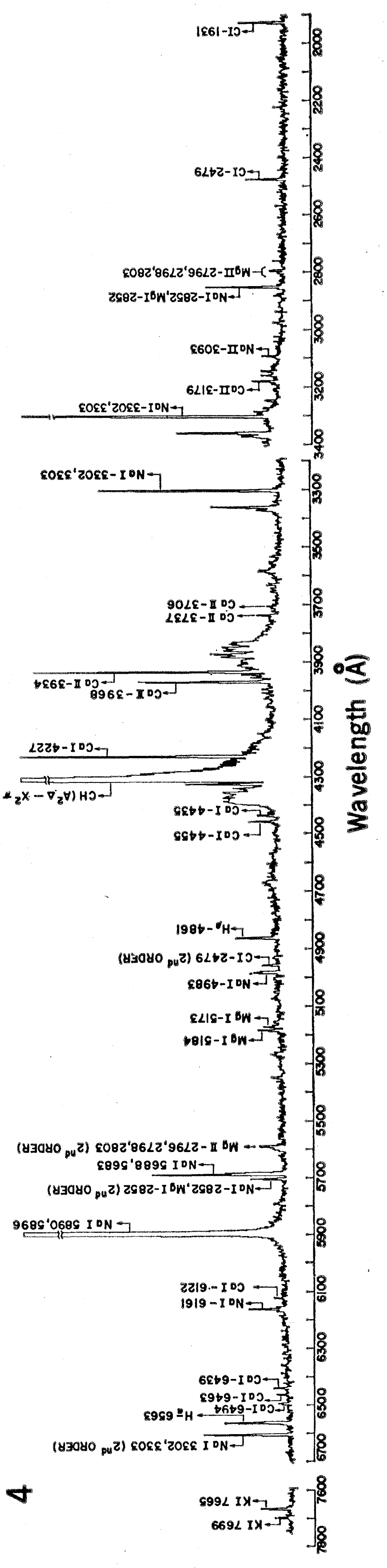
5600
5800
6000
6200
6400
6600
6800
7000
Wavelength (Å)

4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CI-2479
MgII-2796,2798,2803
NaI-2852,MgI-2852
NaII-3093
CaII-3179
NaI-3302,3303
NaI-3302,3303
Ca II-3706
Ca II-3737
Ca II-3934
Ca II-3968
CaI-4227
CH (A²Δ – X²π)
CaI-4435
CaI-4455
Hβ-4861
CI-2479 (2nd ORDER)
NaI-4983
Mg I-5173
Mg I-5184
Mg II-2796,2798,2803 (2nd ORDER)
Na I 5688,5683
NaI-2852,MgI-2852 (2nd ORDER)
Na I 5890,5896
Ca I-6122
Na I-6161
CaI-6439
CaI-6463
CaI-6494
Hα 6563
Na I 3302,3303 (2nd ORDER)
KI 7665
KI 7699
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6700
7600
7800
Wavelength (Å)

quire new and more sensitive analytical techniques. Since the SCANIIR technique samples only a few monolayers of surface material and is sensitive to many of the elements of interest in the blood, we have applied this technique to blood sample volumes ranging from 10 microliters to 0.1 microliter.

Liquids in the form of blood plasma, whole blood, and digested whole blood have been used. Whole blood samples were prepared by depositing one drop of whole blood on a clean quartz substrate immediately after obtaining the sample. The remaining portion of the initial blood sample was allowed to clot and was then centrifuged, and the plasma sample was withdrawn from the liquid component. Digested blood was prepared by diluting whole blood with an excess of ultrapure perchloric acid (4 : 1). This mixture was heated at the boiling point of perchloric acid for approximately 2 hours, and digestion was assumed to be complete when the boiling mixture became colorless.

Radiation which results when N_2^0 at 3.5 kiloelectron volts bombards a quartz disk coated with one drop of blood plasma (approximately 10 microliters) is shown in Fig. 4. The equivalent neutral current was 3×10^{-7} ampere, and gratings blazed at 3000 and 5000 angstroms were used over the spectral range from 1900 to 7700 angstroms. In this wavelength range, radiation was observed from sodium, calcium, potassium, magnesium, carbon, hydrogen, and CH. The radiation from carbon, hydrogen, and CH is assumed to result from the radiative de-excitation of sputtered protein fragments. Silicon radiation, which is characteristic of the quartz substrate, was not observed. This result suggests that the solid residue from 10 microliters of plasma forms a layer whose thickness is large in comparison to the penetration depth of the projectile. After more than 10 hours of continuous bombardment at this energy and current, there was still no evidence of silicon radiation. Essentially the same spectral distribution was observed when the plasma was diluted by a factor of 100 in deionized water and 10 microliters of this solution was allowed to dry on the substrate. This finding indicates that no more than 0.1 microliter of plasma deposited uniformly is required for this qualitative analysis.

Fig. 3 (opposite top). Radiation produced by the impact of N_2^0 (3.5 kiloelectron volts) on (A) volcanic glass and (B) a tektite. Only prominent optical lines are identified in these scans, and these are labeled by element and wavelength. Roman numerals I and II refer to neutral and singly ionized atoms, respectively. Slightly different slit settings were used for the two scans, 125 μm for volcanic glass and 160 μm for the tektite. Fig. 4 (opposite bottom). Radiation produced by the impact of N_2^0 (3.5 kiloelectron volts) on blood plasma.

Metals, such as iron, zinc, and copper, which are also found in trace quantities in blood plasma, have not been positively identified in the spectral scan of Fig. 4. The surface density of these elements in the residue is presumed to be significantly less than that of the organic material and the more abundant metals sodium, potassium, calcium, and magnesium. In addition, major nonmetal constituents, such as chlorine, phosphorus, and sulfur, are not detected in the wavelength interval 1900 to 7700 angstroms. The lowest excited states of these elements give rise to shorter wavelength radiation in the vacuum ultraviolet region.

The spectrum of dried whole blood contained the same optical lines as that of the plasma, with the addition of very weak iron radiation. Most of the iron in blood is found in the red cells, and the iron concentration within the penetration depth of the projectile presumably is larger in the whole blood sample than in the plasma. However, the spectral distribution of radiation from the whole blood sample was observed to change as a function of sputtering time; that is, the intensity of the optical lines arising from magnesium and calcium decreased as a function of time whereas the intensity of the hydrocarbon radiation either remained constant or increased. This finding suggests that magnesium and calcium were being depleted from the surface by the impinging neutral beam, leaving a surface composed principally of red cells or cell fragments.

In order to circumvent the problem of surface depletion and to examine a sample containing inorganic elements found in the walls and interiors of red cells, digested blood was examined. Intense radiation from the decay of excited states of iron, sodium, potassium, magnesium, and calcium was observed when a target containing the residue of this sample was bombarded with N_2^0 at an energy of 3.5 kiloelectron volts. No radiation was observed from excited states of carbon or CH, an indication that the digestion of the organic material was nearly complete. Similar experiments on a quartz disk coated with boiled perchloric acid alone showed that the digested sample was not contaminated with impurities from the perchloric acid or with impurities acquired by the leaching of the quartz containers used in the digestion process. In addition, the intensity of potassium radiation in the digested blood sample was observed to be more than an order of magnitude larger (relative to that of sodium, calcium, and magnesium) than that observed in the radiation scan of blood plasma (Fig. 4). The concentration of potassium in erythrocytes is reported to be approximately 20 times that found in blood plasma (*9*), and this fact probably accounts for the enhanced potassium signals from digested whole blood. A similar enhancement in potassium radiation from blood plasma samples was observed when fresh whole blood was inadvertently centrifuged before clotting, producing hemolysis. Experiments with digested blood plasma gave results similar to those shown in Fig. 4, thus confirming that an enhanced potassium concentration resulted from the digestion of organic material in whole blood.

Detection Sensitivities

The spectrum of collision-induced radiation from a silicate melt target containing known concentrations of impurities has been recorded to determine the detection sensitivities that can be obtained by use of the SCANIIR technique. A homogeneous silicate melt sample (about 82 percent SiO_2) prepared by the Corning Glass Works (*10*) contained known oxide impurities which are listed in column 1 of Table 1. The requested weight fraction of each oxide is listed in column 2; the weight fraction determined by electron microprobe analysis is given in column 3. Concentrations determined by x-ray fluorescence were in substantial agreement with those determined by microprobe analysis except for magnesium oxide and sodium oxide. To remove major surface impurities, the target was washed in xylene, acetone, and deionized water prior to insertion in the apparatus.

We recorded the spectrum of collision-induced radiation which resulted

Table 1. SCANIIR measurements of impurities in a silicate melt.

Impurity	Desired weight fraction	Microprobe weight fraction	Observed optical line	S/N	Concentration for $S/N = 1:1$
Al_2O_3	0.095	0.095	Al I-3962 Å	1400 : 1	6.8×10^{-5}
FeO	.035	.030	Fe I-3720 Å	40 : 1	7.5×10^{-4}
CaO	.010	.0055	Ca II-3934 Å	110 : 1	2.0×10^{-5}
MgO	.012	.009	Mg I-2852 Å	90 : 1	1.0×10^{-4}
K_2O	.012	.0125	K I-7665 Å	15 : 1	8.3×10^{-4}
Na_2O	.012	.008	Na I-5890 Å	340 : 1	2.4×10^{-5}

when N_2^0 (3.5 kiloelectron volts) bombarded the target by scanning selected wavelength intervals under the following experimental conditions: an equivalent neutral current of 3×10^{-7} ampere, monochromator slits 150 μm wide (about 4-angstrom resolution), a grating blazed at 5000 angstroms, a photon integration time of 10 seconds, and a photon counting efficiency (photons counted per emitted photon) of approximately 1 part in 10^5 at 5000 angstroms. From the experimentally measured spectrum of radiation, signal-to-noise ratios (S/N) were determined for the most prominent optical line characteristic of each impurity. These optical lines are listed in column 4, and the measured S/N ratios are given in column 5 of Table 1. The impurity concentration necessary for observation with a S/N ratio of 1:1 at this current and energy in the experimental configuration used is given in column 6 of Table 1. These values were obtained from the ratio of the impurity concentrations (electron microprobe determination) to the measured S/N ratios since, at a fixed beam energy, the optical intensity in a given line is proportional to the product of the beam current and the impurity concentration within the penetration depth of the projectile. Under the outlined experimental conditions, the detection sensitivities vary from a few parts in 10^5 to a few parts in 10^4.

The detection sensitivity for potassium is somewhat less, presumably because the efficiency of the phototube is decreased (relative to peak efficiency) by an order of magnitude at 7665 angstroms. In the case of iron, a large number of lines (more than ten) with nearly equal intensities are observed. The result is that the total optical information is dispersed over a large number of lines and the available signal in a single line is decreased.

For sodium the two most prominent optical lines are at 5890 and 5896 angstroms. In this sample, these lines are separated from any other prominent lines by at least 100 angstroms. Experimentally we observe that increasing the width of the monochromator slits by a factor of 10 results in an improvement of an order of magnitude in the S/N ratio. Thus a detection sensitivity of approximately 1 part per 10^6 can be achieved for sodium in this type of sample with an equivalent neutral current of 3×10^{-7} ampere and a 10-second photon integration time.

The detection limits for this sample can be improved in a number of other ways. One way is to use narrow-band interference filters in place of the monochromator to isolate prominent optical lines emitted by the sputtered impurity atoms. Preliminary measurements indicate that an improvement of a factor of 40 for all the impurities in this sample can be realized by this change alone. An improvement of a factor of 40 results in a detection sensitivity of 6 parts in 10^7 for sodium in this homogeneous sample. Further improvement can be achieved by increasing the neutral beam intensity, by increasing the photon collection efficiency, and by increasing the photon integration time. With these improvements, detection sensitivities of better than 1 part in 10^8 might be achieved in a homogeneous sample.

Summary

When surfaces are bombarded by low-energy ions and neutrals, a significant number of sputtered atoms and molecules leave the surface in excited electronic states. Optical emission lines, which result from the decay of these excited states, provide the basis for a technique for the identification of surface species. Experimental results presented here demonstrate that with the SCANIIR technique, which is based on the excited-state sputtering phenomena, one is able to detect a large variety of surface constituents and contaminants by the identification of the characteristic optical radiation produced when low-energy neutrals bring about the sputtering of surface atoms and molecules. Detection limits for trace impurities in the silicate melt in these experiments range from 8.3×10^{-4} to 6×10^{-7}. Preliminary evidence indicates that in a homogeneous bulk sample detection limits for trace impurities can be lowered to 10 parts per 10^9 by increasing the photon collection efficiency and by increasing the neutral flux. Because of its sensitivity as a surface probe, and because only very small quantities of material are required for analysis, it seems likely that the SCANIIR technique will become an important tool for surface analysis with application to scientific, technological, and environmental problems.

References and Notes

1. C. W. White and N. H. Tolk, *Phys. Rev. Lett.* **26**, 486 (1971).
2. C. W. White, D. L. Simms, N. H. Tolk, in preparation.
3. See, for example, M. Kaminsky, *Atomic and Ionic Impact Phenomena on Metal Surfaces* (Academic Press, New York, 1965).
4. H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Clarendon, Oxford, 1952).
5. C. A. van de Runstraat, R. Wijnanendts van Resandt, J. Los, *J. Sci. Instrum.* **3**, 575 (1970).
6. Radiation from sputtered surface atoms and ions has been observed at much higher ion beam energies (above 5 kiloelectron volts). [See, for example, J. M. Fluint, L. Friedman, J. Van Eck, C. Snoek, J. Kistemaker, in *Proceedings of the Fifth International Conference on Ionization Phenomena in Gases, Munich, Germany, 1961*, H. Maecker, Ed. (North-Holland, Amsterdam, 1962); C. Snoek, W. F. Van der Weg, P. K. Rol, *Physica Utrecht* **30**, 341 (1964); W. F. Van der Weg and D. J. Bierman, *ibid.* **44**, 206 (1969); I. Terzić and B. Perović, *Surface Sci.* **21**, 86 (1970); P. J. Meriaux, R. Goutle, C. Guillaud, paper presented at the international meeting on Chemical Analysis by Charged Particle Bombardment, Namur, Belgium, September 1971; I. S. T. Tsong, *Phys. Status Solidi A* **7**, 451 (1971)]. Sputtered excited atoms also are believed to contribute to the radiation observed in glow discharge experiments involving cathode sputtering of oxide films [see, for example, H. Sporn, *Z. Phys.* **112**, 278 (1939)].
7. Thermal electrons can be used to reduce charge accumulation on nonconducting surfaces bombarded with ions. However, this procedure may influence ion neutralization processes and collisional excitation processes.
8. This statement applies only to ions whose ionization energy is large in comparison to the work function of the metallic target [H. D. Hagstrum, *Phys. Rev.* **96**, 336 (1954); *ibid.* **123**, 758 (1961)].
9. P. M. Hald, *J. Biol. Chem.* **163**, 429 (1946); R. Synder and S. Katzenelbogen, *ibid.* **143**, 223 (1942).
10. We thank Dr. L. S. Walter, Geochemistry Laboratory and Laboratory for Theoretical Studies, Goddard Space Flight Center, Greenbelt, Maryland, who lent us the silicate melt. For further details on this sample, please see: L. S. Walter and J. E. Guitronich, *Sol. Energy* **11**, 163 (1967).
11. We thank R. P. Watts, Huntsville, Alabama, who lent us the tektite and volcanic glass samples.