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INTENSE BEAMS OF RADIOACTIVE HALOGENS PRODUCED
BY MEANS OF SURFACE IONIZATION

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ABSTRACT

A negative surface-ionization source has been developed for on-line separator use in order to make intense ion beams of nuclear-reaction produced halogens. It consists of a planar LaB_6 surface onto which the mixed volatile nuclear reaction products are allowed to impinge. A transverse permanent magnetic field and an intermediate electron catcher electrode, inserted before the separator extraction gap, is used to separate the ion and electron fractions. The efficiency of the source is shown to be up to 50% for the halogens, Br and I, i.e. very similar to that obtained by the same process for positive ionization of alkalis on a tungsten surface.

During periods of several weeks the source has been used for a number of on-line experiments and has allowed the identification of a series of new nuclei. Yields and half-lives of $^{42,43}\text{Cl}$ and $^{70,71,72\text{m},76\text{m},93,94}\text{Br}$ are reported.

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1. INTRODUCTION

Up to the present time, methods for on-line isotope separation of about 40 nuclear-reaction produced elements have been developed at ISOLDE ¹⁾. For 22 of these elements intense ion beams, uncontaminated by isobars from neighbouring Z elements, are available for studies. This selectivity is achieved by proper combination of target materials^{2,3)} plasma-discharge ionization^{1,4,5)} and positive surface ionization⁵⁾. By application of the negative surface ionization effect a new class of isotope-separated beams can be obtained, making use of the high selectivity of this process that forms negative ions of the halogens. This was demonstrated early on by Venezia and Amiel⁶⁾. In their off-line separation of iodine, ionization yields of only $10^{-4}\%$ were obtained, presumably owing to the high work-function of the graphite emitter used. Also in the on-line separations of Br and I, by Reeder et al.⁷⁾, low yields were obtained from their UO₂-graphite surface.

The present paper describes how the use of low work-function thermoionic emitter surfaces allows the development of a negative surface-ionization source for on-line separation of Cl, Br, and I with efficiencies of up to $\sim 50\%$. In combination with different target materials the source has proved, in a number of on-line experiments⁸⁻¹⁰⁾, to be as efficient and reliable as experienced with positive surface ionization of the alkalis on a tungsten surface. The performance of the source is described in terms of production yields, ionization efficiencies, and delay-time distributions. The new region of nuclei far from stability made accessible by this technique is illustrated by the half-life determination of a number of newly identified nuclei.

It now seems possible to extend negative surface ionization to a number of elements less electronegative than the halogens. For this purpose, surfaces with work-functions down to ~ 1 eV, as reported in the literature, may be needed. The very high yields of negative molecular ions formed by surface ionization may be an alternative method.

2. GENERAL PRINCIPLES OF THE NEGATIVE SURFACE IONIZATION PROCESS

The degree of negative surface ionization is described by an expression similar to the well-known Saha-Langmuir formula

$$\alpha = \frac{g_-}{g_0} \exp \left(\frac{A - \phi_0 + f(E) - c\theta}{kT} \right), \quad (1)$$

where g_- and g_0 are statistical weight factors describing the number of states accessible, respectively, in the negative ion or the neutral atom, weighted by their Boltzmann's factor at the actual temperature, A is the electron affinity (eV), ϕ_0 the "clean" surface work-function (eV), $f(E)$ the Schottky effect¹¹⁾ describing the diminution in ϕ with increase in the electrical field E , θ the degree of monolayer surface coverage, k the Boltzmann constant, T the absolute temperature (K), and c a constant that may be positive or negative. Partial surface coverage with a low or a high work-function material may, respectively, decrease or increase the effective work-function^{12,13)}. In cases where the Schottky effect and the surface coverage effect can be neglected, a high degree of ionization is obtained when $\phi_0 < A$.

For proper operation in an on-line isotope separator, additional demands of the surface are that operation can take place at elevated temperatures (in order to minimize the delay-time loss in this step for short-lived nuclides), that it has a low vapour or decomposition pressure, that it is chemically inert, and that it has high enough electrical conductivity to ensure a fast replacement of the electrons removed from the surface in the ionization process.

3. CHOICE OF IONIZER

The electron affinity of the halogens is always greater than 3 eV¹⁴⁾, except for At (2.8 ± 0.2 eV)¹⁵⁾. Hence a surface with $\phi < 2.8$ eV will ensure a high degree of ionization for these elements. Results are reported for different surfaces which have been tested for negative halogen-ion formation. Examples are Cs¹⁶⁾, carburized thoriated tungsten¹⁷⁾ and GdB₆¹⁸⁾. But the most promising

material is LaB_6 , of which the thermoionic properties have been extensively investigated¹⁷⁻²⁴). A survey of measurements of its work-function shows a range of values from 2.36 eV to 3.3 eV, with the majority of values around 2.7 eV. The spread in the values most probably reflects the effect of surface poisoning, which can be quite pronounced for low work-function surfaces^{13,25,26}). After promising off-line tracer ionization with radioactive ^{131}I , LaB_6 was chosen as the emitter material for the halogen experiments. This material is refractory and stable up to 1500 °C in vacuum, should not react appreciably with halogens, and has a low resistivity.

4. CONSTRUCTION AND CHARACTERISTICS OF THE TARGET AND ION-SOURCE COMBINATION

The principle and construction of the source is shown in fig. 1. The negative ion emitter consists of a porous pellet, 2 mm in diameter and 2 mm thick, contained in a cavity in a tantalum holder. The pellet is prepared simply by pressing the dry LaB_6 powder by hand into the cavity, followed by a sintering in vacuum at 1800 °C for 15 min. The pellet holder is inserted into the extraction end of the tantalum transfer tube which forms the connection to the target. The volatile nuclear reaction products, carried away from the target by thermal diffusion through the ohmic heated transfer tube, impinges onto the emitter surface with a geometrical probability of $\sim 50\%$. The ions formed are extracted by the extraction electrode, kept at a potential of 20 kV. In order to avoid the acceleration of the abundantly emitted electrons to the 60 kV potential of the separator they are deflected onto a separate powered electrode kept at a potential of ~ 1 kV. The deflection is obtained by means of an 800 G permanent magnet field.

A characteristic property of the LaB_6 emitter is its sensitivity to poisoning by absorbed impurities¹³). It therefore needs an activation by heating for some minutes to 1500-1600 °C each time it has been exposed to the atmosphere. The degree of activation can be followed by measuring the electron emission, which reaches about 10 mA in the present set-up. The negative ion beam yield measured with $^{76\text{m}}\text{Br}$ ($T_{1/2} = 1.35$ s) as a function of emitter temperature shows a pronounced maximum

at ~ 1260 °C. This behaviour may be understood as the efficiency variations for a porous emitter described by Pelletier et al.²⁷⁾, who showed that the efficiency increases as a function of decreasing surface coverage, followed by a decrease when, at high temperature, the diffusion of the halogen in the porous system changes from surface diffusion to volume flow.

Two targets have been used in these experiments: a niobium powder target²³⁾ containing 131.6 g Nb (thickness 85.2 g/cm²) and a UC-graphite target⁵⁾ with 84.5 g ²³⁸U (thickness 54.9 g/cm²) where the amount of uranium constitutes approximately 10% of the atoms in the target matrix. It is well known from off-line studies that halogens are released efficiently from both these targets^{2,3)}. The target layout is described in ref. 2.

5. RESULTS

5.1 Delay-times

The delay-time is the time that has elapsed between production and detection of a nuclide. It can usually not be quantitatively described in terms of a simple constant or average value for a given system. It must be represented by a delay-time distribution-function, as discussed in refs. 1, 3, and 5. Only from a knowledge of the shape of this function can conclusions be drawn about the delay-time losses of short-lived nuclei and the release mechanisms. It is often difficult to measure this function accurately and a more simple readily-measurable quantity, the delay half-time $(t_d)_{\frac{1}{2}}$ ²⁸⁾ may be used qualitatively to describe the speed of the system. It expresses how fast the constant production yield of a given nuclide is halved after the proton beam is switched off²⁹⁾. The $(t_d)_{\frac{1}{2}}$ value indicates whether or not there is an appreciably fast component in the diffusion mechanism.

For the presently used Nb powder target ($t = 2100$ °C) for production of Br it was found that at low transfer line temperature (< 1000 °C) the delay-time distribution as measured with ^{76m}Br showed a line-temperature-dependent single exponential behaviour²⁸⁾ with $(t_d)_{\frac{1}{2}} = 169$ s. At higher line-temperature (1300 °C) the distribution changes into a function which is best described by a sum of exponentials

with $(t_d)_{1/2} = 25$ s. Off-line measurements with stable Br showed that at low line temperatures the over-all delay is determined by desorption of Br from the line and ionizer surfaces. This partial delay could be reduced to $(t_d)_{1/2} \sim 3$ s at a temperature of ~ 1500 °C. In combination with the UC-graphite cloth target⁵⁾ kept at 2100 °C and a line-temperature of > 1600 °C a $(t_d)_{1/2}$ value of ~ 2 s was found for the release of ^{85}Br . This is as short as the release of Rb and Cs from the same target matrix⁵⁾. The delay-time distribution and $(t_d)_{1/2} = 25$ s for the release of Br from the Nb powder target is caused by the combined effect of a lower line temperature and a slower release from this matrix. No systematic study of the delay of Cl has been made but the steep slope of the yield curve discussed in section 5.2 indicates a somewhat longer delay. Most likely it originates on the line and ionizer surface, since off-line measurements³⁾ of Cl release from high-temperature target materials shows a particularly rapid release of Cl.

5.2 Production yields

Production yields are determined for bromine from the Nb-powder target and for chlorine and bromine from UC-graphite target. These are illustrated in figs. 3-5. The experimental points are not corrected for decay according to the actual delay time distribution, and represent simply the isotopic yields (in atoms/s) at the detection position. The values have been measured by a Faraday cup and a 4π β -detector operated in the multiscaling mode, except for the two nuclides $^{93,94}\text{Br}$ where a ^3He neutron counter was used. A relative yield curve containing the mass numbers 92-94 can be constructed by integration of the peaks in the neutron scan shown in fig. 5 corrected with their p_n values. The p_n value for ^{92}Br is taken from ref. 25, and the p_n -values for $^{93,94}\text{Br}$ are estimated on the basis of a linear fit to the values for $^{87-92}\text{Br}$ ²⁵⁾. This yield curve is then normalized to the yield of ^{92}Br measured by the β -counter.

So far no complete yield curve has been determined for iodine. But the two isotopes measured, $Y_p(^{137}\text{I}) = 3.5 \times 10^7$ atoms/s and $Y_p(^{140}\text{I}) = 3.1 \times 10^5$ atoms/s, point to a yield curve maximum probably around mass 131-132 of about the same magnitude as the one presently given for bromine.

By comparing the Cl yields in fig. 3 with those of K from the same target¹⁾ it is striking that the slope of the Cl curve is much steeper than that of K. This effect could be due to pronounced delay-time losses of the short-lived nuclei.

The elements fluorine and astatine could not be found in the mass spectra at their respective atomic masses although they were expected to be released from the target. The formation of non-ionized chemical compounds or molecular sidebands is however possible, but no systematic search for sidebands has been carried out, to date.

5.3 Ionization efficiencies

The ionization probability of the halogens which impinge on the LaB₆ surface is according to eq. (1) close to unity. The expected ionization efficiency of the present source arrangement should therefore be $\sim 50\%$, since the probability that the atoms strike the LaB₆ is $\sim 50\%$, as discussed in section 4. By comparing the production rates of Br in the Nb target with the obtained yields shown in fig. 4, an efficiency of $73 \pm 25\%$ was found, in agreement with the expectations.

However, in combination with the UC-graphite target the Br ionization efficiency determined by the same method gives only 1%. Furthermore this efficiency continuously decreases but could be restored by reforming the ionizer as described in section 2. This is taken as a clear sign of poisoning of the ionizer, presumably by carbon which is being outgassed abundantly from the target as CO. In fact Avidenko and Malev¹³⁾ have demonstrated the sensitivity of LaB₆ to carbon contamination.

The ionization efficiency for Cl at present reaches only a few per mille, most likely owing to the combined effect of poisoning of the emitter surface and formation of molecular compounds.

5.4 Identification of new halogen isotopes

The first successful on-line use of the negative surface-ionization source allowed the extension of the region of halogen isotopes to a number of new and previously poorly known nuclei. Results from preliminary radioactivity measurements on ^{42,43}Cl and ^{70,72m,76m,93,94}Br are summarized in table 1. The

half-lives are all determined by multiscaling of the β -ray activity and computer resolution of the decay curves. At mass 70 a nuclide which decayed with a half-life of 2.1 s was identified. This value is different from the half-life of 80 ms determined by Alburger et al.²⁹⁾ for ^{70}Br and indicates that isomerism might exist in this nucleus. The half-lives of the two low-energy γ -rays at mass 76 are both determined to 1.3 s by multi-spectrum analysis of the γ -ray activity. They are reported³⁰⁾ to be coincident and interpreted as the isomeric transition.

6. CONCLUSION AND OUTLOOK

This test constitutes the first successful adaptation of a surface-ionization source to an on-line mass separator for selective production of negative ions in high yields from a complex nuclear reaction mixture. This is demonstrated by the extracted beams of the halogens, chlorine, bromine, and iodine. The efficiencies for Br and Cl, affected by poisoning when released from a carbide target, may be increased if carbon-free targets are used. Two such high-temperature targets are at present under study; Ta powder for fragmentation production of Cl and ThO_2 for production of the neutron-rich Cl, Br, and I. The long delay-times for Cl may be due to the higher chemical stability of the chlorides, which prevents their dissociation and desorption from the line or ionizer surfaces. Higher line temperature combined with an ionizer like ZrC that operates at high temperature may solve this problem. Furthermore, this measure could increase the possibilities of making radioactive beams of fluorine, which is the halogen that forms the most stable compounds.

A number of elements have electron affinities in the range 2.8-1.8 eV¹⁵⁾ such as Au (2.80 eV), Pt (2.56 eV), S (2.07 eV), Se (2.12 eV), and Ag (2.0 eV)^{15,31)}, for which promising target materials also exist. Efficient negative ionization may be extended to these elements in case surfaces with $\phi < 1.8$ eV can be found. In fact, such surfaces are reported to exist either as electropositive layers on a refractory metal like W-Ba ($\phi = 1.6$ eV)²⁶⁾ or mixed oxides such as SrOBaO

($\phi = 1$ eV)²⁶⁾. From the latter surface an S^- beam of the order of 1 μ A was obtained in preliminary work³²⁾. The reproducibility of the low work-functions still remains to be verified, since they are likely to be sensitive to poisoning.

Recent observations have demonstrated that remarkably high molecular electron affinities are observed for several hexafluorides³³⁾. The $E_A(UF_6) \approx 5.1$ eV allows a 100% efficient surface ionization. Also in the present experiments a number of negative molecular ions have been observed. Regardless of whether they have been formed in surface ionization or secondary effects, they may offer possibilities for selective ionization of a number of elements.

It seems that the results reported here indicate interesting prospects for the future, not only as regards selective on-line separation but also for a more general ionization method to be used in other fields.

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Table 7

Nuclear data on some new and poorly known halogen isotopes

Nuclide	Half-life measured (s)	Number of half-lives followed	Other radiation	Literature quotations
^{42}Cl	6.8 ± 0.3	6	n-emission not detectable	-
^{43}Cl	3.3 ± 0.2	5	n-emission not detectable	-
^{70}Br	2.2 ± 0.2	10	not measured	$t_{1/2} = 80 \text{ ms}$ ²⁹⁾
^{71}Br	21.5 ± 0.5	6	not measured	-
$^{72\text{m}}\text{Br}$	7.2 ± 0.5	5	Delayed p-branch of $6 \times 10^{-7} \text{ a}$)	$t_{1/2} = 1.3 \text{ min}$ ³⁰⁾
^{72}Br	73.2 ± 0.5	7		
$^{76\text{m}}\text{Br}$	1.35 ± 0.05	6		$t_{1/2} = 1.49 \pm 0.02 \text{ s}$ ^{c)}
			γ emission (keV) ^{b)} :	γ emission (keV):
			44.5 ± 1.0	45.48
			56.6 ± 1.0	57.11
^{93}Br	not measured		n-emission	-
^{94}Br	not measured		n-emission	-

a) The origins of the proton-emitting levels are at the moment not clear.

b) The large error limits are due to the simple energy calibration with the two X-ray lines in lead $K_{\alpha 1}$ (74.97 keV) and $K_{\beta 1}$ (84.94 keV).

c) W.D. Schmidt-Ott, A.J. Hautojärvi and U.J. Schrewe, Z. Phys. A289, 121 (1978).

Figure captions

Fig. 1 : The principle and the technical details of the negative surface-ionization source.

1. Permanent magnet	5. Electron catcher electrode
2. Pole-piece	6. Insulator
3. Ionizer constriction	7. Mounting plate
4. Product transfer line	

Fig. 2 : Yields of Cl isotopes as Cl^- from a 600 MeV proton-irradiated UC-graphite target. The points correspond to a uranium target thickness of 54.9 g/cm^2 and a proton beam intensity of $1 \mu\text{A}$. The full curve is drawn to guide the eye.

Fig. 3 : Yields of Br isotopes as Br^- from a 600 MeV proton-irradiated UC-graphite target. The points correspond to a uranium target thickness of 54.9 g/cm^2 and a proton beam intensity of $1 \mu\text{A}$. The curve is drawn to guide the eye.

Fig. 4 : Yields of Br isotopes as Br^- from a 600 MeV proton-irradiated Nb-powder target. The points correspond to a target thickness of 85.2 g/cm^2 and a proton beam intensity of $1 \mu\text{A}$. The points marked m are only isomeric yields and the curve is drawn to guide the eye.

Fig. 5 : Mass scan on heavy Br^- isotopes obtained by means of an integral ^3He neutron counter.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5