# Spectroscopic analysis of the blue light emitted from Middleton type Cesium sputter negative ion sources.

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To unravel the mechanisms of ion formation in the Middleton type cesium sputter negative ion source, we have acquired and analyzed the spectrum of the light emitted from the source region during sputtering of three different cathode materials; carbon, aluminum and copper. All cathodes were analyzed under the same source settings but with different total current output. The cathode region was observed from a distance of 3 meters and the emitted light was analyzed by a fiber coupled spectrometer with a wavelength range from 350 to 1100 nm. The spectra showed clear differences depending on the cathode material. The emitted light from the carbon cathode consisted almost entirely of lines from neutral cesium and no lines from ionized cesium. Both metallic cathodes additionally displayed several lines originating from positively ionized cesium. A weak, broad feature between 470 and 510 nm was also seen in the carbon spectrum. This feature was not present in spectra from the two metallic cathodes. These results may suggest different mechanisms of negative ion formation in the ion source depending on the cathode material. As a side effect of the measurement it proved relatively easy to determine the source temperature, in the range 1020 K to 1215 K depending on source settings, to an accuracy of ± 30K from the black body radiation.

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## I. INTRODUCTION

Negative ions of atoms and molecules are widely used both in the fundamental and the applied research. The possibility to provide stable beams of negative ions is important in negative ion research [1], fusion development [2] and nuclear physics performed with tandem accelerators [3]. A special case of the last is ultra rare isotope analysis by Accelerator Mass Spectrometry (AMS) [4]. Sputter ion sources of the Middleton type [5] have since 1977 been the main tool used to create stable, intense negative ion beams for injection into AMS machines. In this type of ion source, the sample acts as the source's cathode and is placed in a holder made of a suitable metal at the back end of the source. Cesium vapor is admitted into the source, some of which is deposited onto a surface ionizer, positioned in front of the sample holder and set on a potential usually 2-12 kV above the cathode. Positively ionized cesium is accelerated and focused onto the cathode and sputters fragments from the sample. The sputtered particles acquire electrons from the cesium, present both as a thin layer on the cathode surface or as vapor inside the evacuated source. These negative ions are then accelerated by the potentials in the source, pass through a hole in the ionizer and are extracted from the source for further acceleration. Many atomic and molecular negative ions can be produced in this kind of sputter source. Despite its long history as a workhorse for negative ion physics, the mechanisms of ion production is not fully known. Little work has been put into understanding the physics of the Middleton source and the ion formation mechanisms is generally thought of as analog to that of negative secondary ionization mass spectrometry (SIMS). However, the exact processes, involving positive and neutral cesium in both its excited and ground states as well as their interactions with the target atoms and the produced negative ions have not been studied and described quantitatively [4].

The electron tunneling model for surface ionization of the sample in SIMS [6,7,8] suggests the lowered work function of the sputtered material by cesium coverage as the main mechanism of successful ion production. The ion formation probability under SIMS conditions is a function of the electron affinity of the sputtered atom and the value of the surface work function:

$$P^{-} \propto exp[-(\Phi - A)/\varepsilon_0] \qquad (1),$$

where $\Phi$ is the surface work function, $A$ is the electron affinity of the sputtered atom and $\varepsilon_0$ varies with the emitted atoms velocity. (See ref [6] for details). SIMS theory states that the ions are formed at very close distance to the surface, where the electrons can tunnel from the surface and attach to the sputtered neutrals. The total ionization efficiency is a function that includes the sputter yield. This explains the SIMS results of a lower total efficiency of gold compared to carbon despite the lower work function of gold. The gold is sputtered faster than the cesium layer is refilled, resulting in a high yield of neutrals. In a Middleton sputter source there should be plenty of cesium around to sufficiently cover the sample at all times and the sputter yield should therefore not affect the ionization efficiency. This is supported by the highly increased ionization efficiency in the case where extra cesium is supplied for a SIMS setup as done by P Philipp *et al.* [9].

An early study of the beam energy distribution from a Middleton type source [10] suggested that, under certain conditions, the ionization by electron tunneling compete with post-ionization taking place in the volume between the surface ionizer and the cathode. In a recently submitted manuscript by J Vogel *et al*. [11], several examples of where the physics in the Middleton sputter source diverge from SIMS theory are presented. An alternative theory based on post ionization is given. It is suggested that ions are formed in front of the cathode, in a volume dominated by Cs neutrals. These are evaporated from the cathode area and charge transfer ionization from their exited states is taking

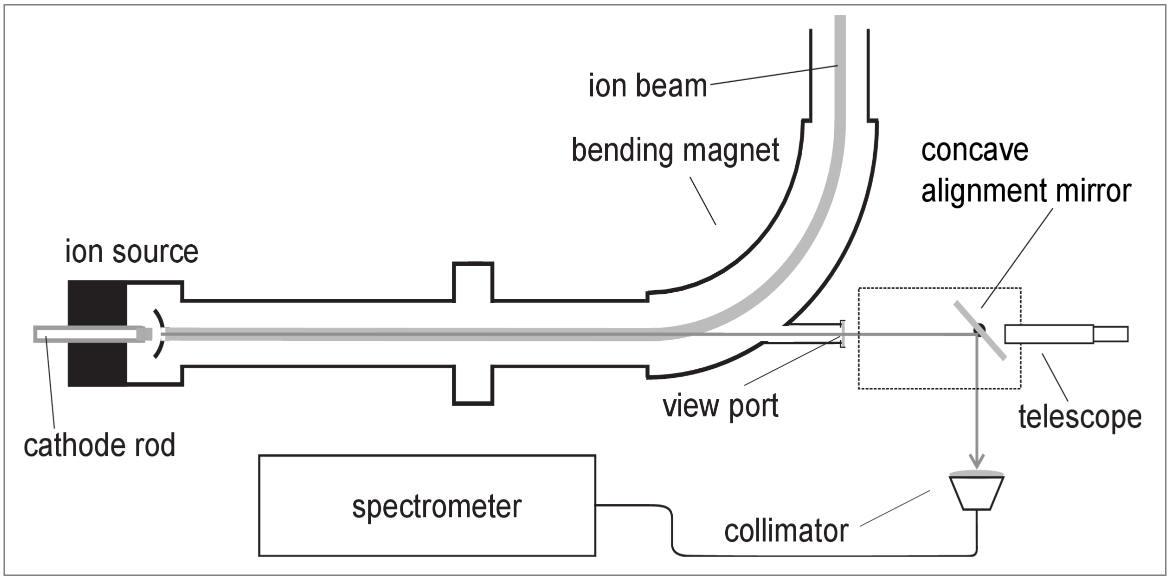


FIG. 1. A graphical representation of the experimental setup.

place in collision with sputtered neutral sample atoms. This volume can be recognized by an emission of blue light originating from de-exciting ${}^{*}$Cs and ${}^{*}$Cs$^{+}$.

Regardless of the ion formation mechanisms, some parameters for a successful production of an intense ion beam are empirically known [12]. The most important of these are the quantity of cesium injected into the source, the power dissipated by the ionizer and the composition of sample material. The most intense beam out from the source is in our experience reached when these parameters are optimized together with a relatively tight focus of the cesium positive ion beam on to the target surface. This can be done either by using an electrostatic lens or by adjusting the distance between the cesium ionizer and the cathode. Fully optimized, a ${}^{12}$C$^{-}$ current of hundreds of µA can be extracted from a graphite target [12]. At such high output, a region emitting blue light can characteristically be seen immediately in front of the sample. This blue light has often been supposed to originate from cesium. Middleton mentions this as, quote: “the formation of a small ball of bright (often pale blue) plasma”[12]. However, the light emitted from a Middleton sputter ion source has, to our knowledge, never been studied spectroscopically.

## II SETUP

The Ion Laser InterAction System apparatus at the Vienna Environmental Research Accelerator (VERA) laboratory is relying on a SNICS II sputter negative ion source (National Electrostatics Corp.) to provide negative ion-beams, primarily for development of isobar separation methods. Parameters of the ion source are monitored and controlled by a dedicated computer program. The three different cathodes used in this experiment were two solid metal cathodes, aluminum and copper, and a copper cylinder with a 6.5 mm diameter hole filled with graphite powder. The Cs Ionizer used was a conical surface ionizer with a diameter of 40 mm with a 6.3 mm central orifice. The cathode surface is approximately 13 mm from the ionizer central orifice, but this distance is usually adjusted within a few mm to maximize source output. All spectra were acquired under as identical source settings as possible: Ionizer power was 185 W, the cathode voltage was 6 kV and the beam was accelerated to 23.5 keV. Cesium oven temperature was 225ºC and our Cs feed line temperature was 140ºC. These settings provided a total output of between 14 - 55 µA, depending on the different cathode materials. The cathode position was adjusted by optical inspection through the view port mentioned below, so that the blue glow was focused to a small bright spot in the center of the cathode. This position always coincided with a high stable total output. The mass selecting magnet of the apparatus has a window that provides a free line of sight straight onto the cathode through the injection beam line. The distance from the cathode surface to the window is 297 cm. The optical path outside the chamber consisted of a F=100 mm concave silver mirror and a collimator corrected for chromatic aberrations which coupled the light into a multimode fiber (Thorlabs AFS50/125Y). The fiber was connected to an Ocean optics QE65000 spectrometer equipped with a 25μm entrance slit and a HC1 grating tuned to a nominal wavelength range of 350 – 1100 nm and with a resolution of 0.8 nm. The concave mirror could be removed and allow for direct inspection and photographing of the cathode through a telescope, see figure 1. (and for online version, figure 1b ). By switching the cathode rod to a Plexiglas rod with a 1 mm aperture at the end, light from a HeNe laser could be emitted from the position of the sample to guide in the setup. After a rough alignment using this aid, the setup could be optimized using the black body radiation from the hot source.

The software of the spectrometer made it possible to directly subtract a spectrum acquired when the cathode voltage was turned off, and hence not being sputtered, from a spectrum where the voltage was turned on, and the sputtering active. Recorded spectra therefore only contain information of light created, directly or indirectly, by the sputtering of the cathode surface. The spectra was calibrated with signals from the HeNe laser (632.992 nm) and a frequency doubled Nd:YVO4 (532.15 nm) laser to a precision of 0.2nm.

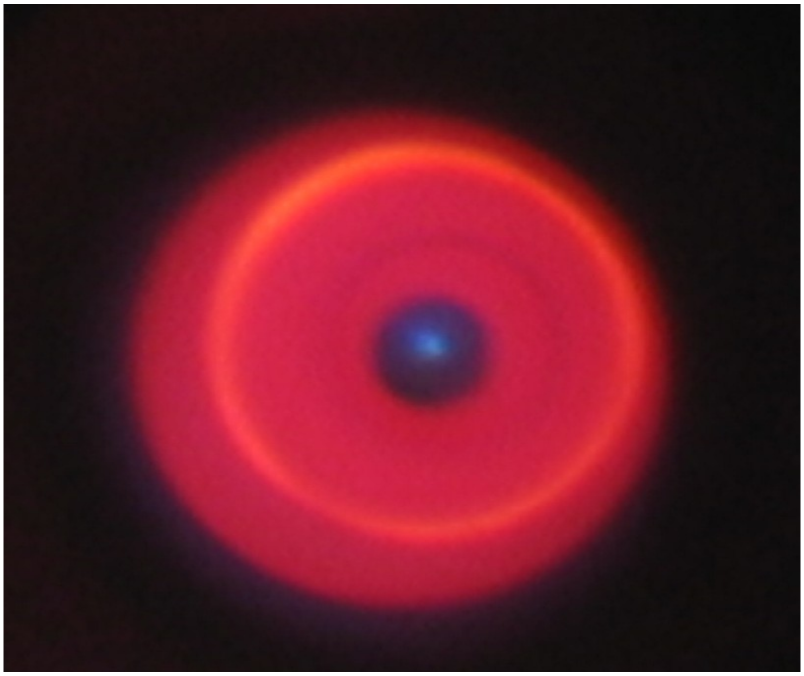


Fig 1B (Color online) The front surface of the of a carbon-loaded cathode seen through a telescope placed in front of the view port on the system. The blue spot in the middle is light emitted when the cathode is being sputtered. The bright red ring is the edge of the tantalum ionizer. The whole region is seen through the source extraction aperture.

## III. RESULTS

The black body radiation from the ionizer and cathode from 400 nm to 825 nm is shown in figure 2. In the inset a damping of the black body radiation at longer wavelengths can be seen. This behavior was reproduced in control measurements of black body radiation from a small tube furnace at temperatures from 1000 – 1200 K. We attribute this to an uncompensated quantum efficiency in the spectrometer CCD. We were nevertheless able to fit Planks law up to ~750 nm with good agreement. From this fit we where able to extract the temperature to an accuracy of ±30 degrees, where the error comes from difference in temperatures extracted depending on the fitted distance and comparison with spectra from a temperature controlled furnace. The solid black line in figure 2 shows Planck's law fitted to the to the signal up to 750 nm. Fitting to higher wavelengths produces larger fitting errors due to the deviation of the spectrum from a true black body radiation. Figure 3 shows part of the spectrum of the light emission from the three different cathodes obtained by subtracting a spectrum with the 6kV cathode voltage turned off, from a spectrum with cathode voltage on. Thus, all light emissions from the ionizer, vacuum gauges and other stray light sources are subtracted.

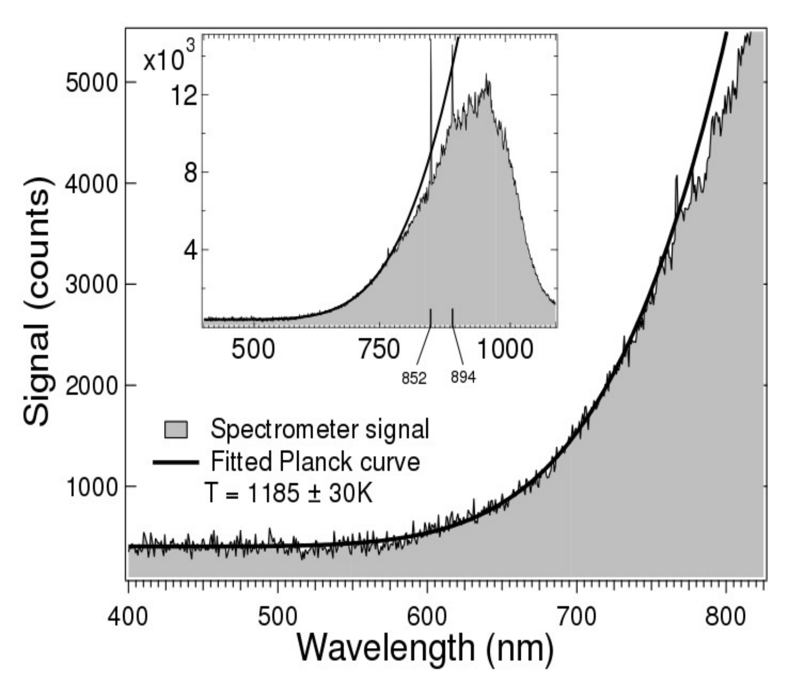


FIG. 2. Black body radiation emitted from the hot source. A fit of Planck's law to the data from 400 to 750 nm gives a temperature of ~1185 K Control experiments have shown that this is accurate to within ±30K. The drop off from the Planck curve is an artifact from the spectrometer. Two strong peaks from neutral cesium can be seen in the inset.

Peak center positions were well defined by fitting with either a Voigt, Lorenzian, and in a few cases, Gaussian profile, depending on the best fit. The uncertainty in these fits were always smaller than the uncertainty in the

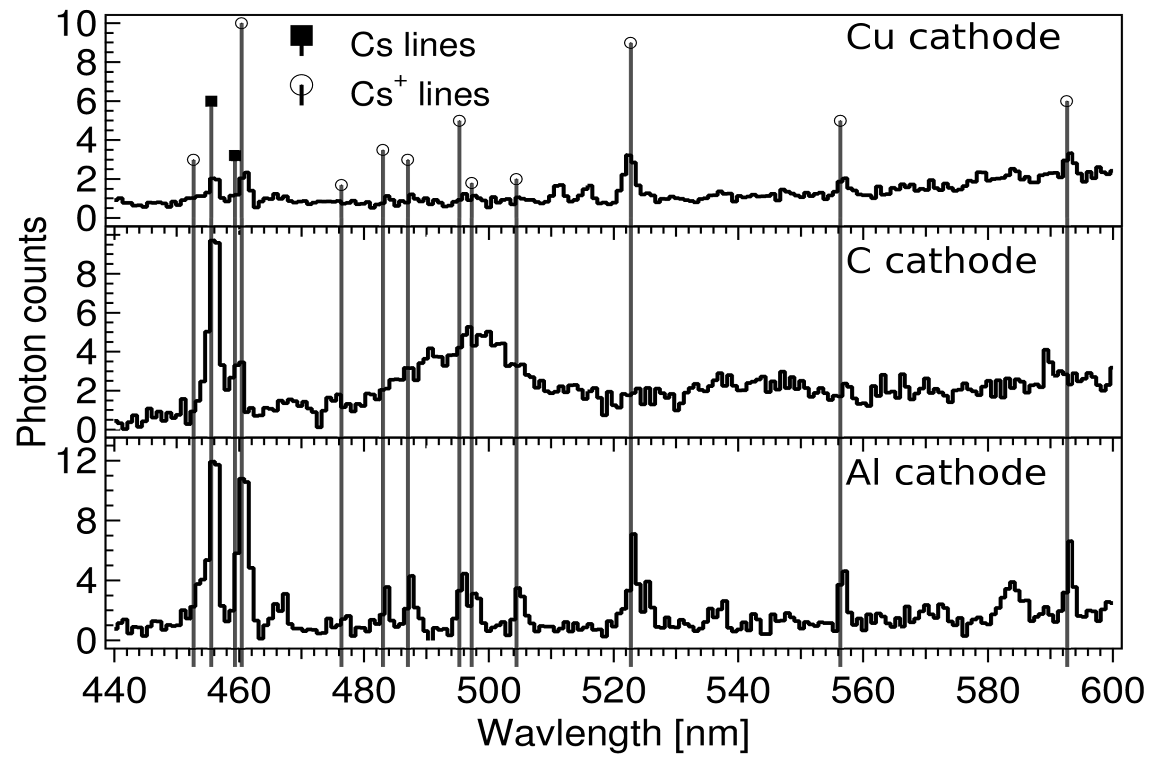
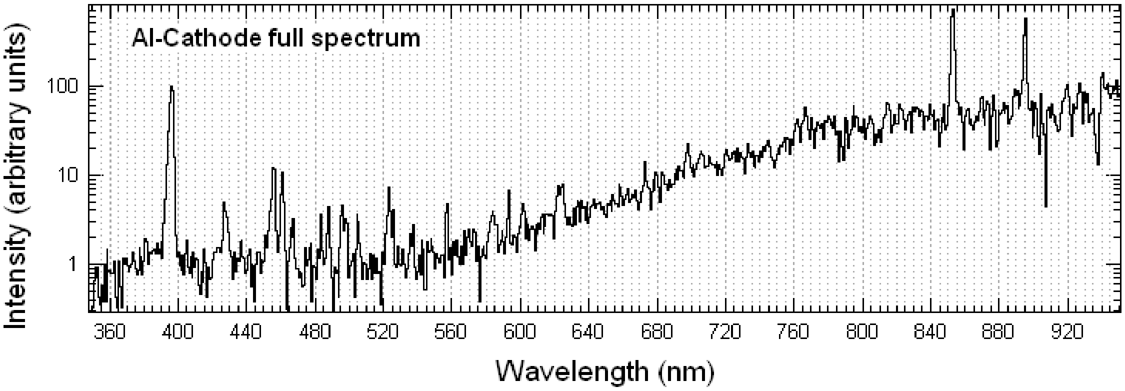


FIG. 3. The resulting spectrum with the blue light ON after a dark spectrum recorded with the cathode voltage turned OFF has been subtracted. Only the part between 440 and 600 nm, responsible for the blue light, is shown here. The light from the copper cathode was much weaker than from the other two. Positions for some Cs and Cs$^+$ lines visible in the spectra are marked.



**F**IG. 3B. The full spectrum of the Al-cathode measurement. The three strongest lines, from Al II and Cs I are on the edge of, respective outside the visible range.

calibration of the wavelength scale. The lines identified in each spectrum are tabulated in appendix 1. The measured relative strengths of the lines within each spectrum are also presented there. All peaks in the tables were normalized to the 455.528 nm Cs-line of each spectrum in order to compare between the different spectra. The two lines above 800 nm are by far the strongest and are visible in the spectra even without background subtraction (see inset fig 2). In the carbon spectrum a weak continuum or a broad peak of uncertain origin can be seen just below 500 nm. If fitted with a Gaussian the center is at 496.9 ± 0.4 nm with a FWHM of ~17 nm. Five separate peaks from $Cs^+$ were found in the same region when the Al cathode was used. For copper the total light output was much weaker and no peaks in this region were visible.

To further examine whether the appearance of blue light at high source output coincides with changes in the mechanism of ion formation, two other tests were performed with the carbon cathode: a comparison of the atomic vs. molecular ion output from the source and an analysis of the high and low energy tails of the $^{12}C$ peak, i. e. the wings of the peak containing ions that is not accelerated by the full potential and ions that in the sputter process acquire a small kinetic energy that is added to the acceleration energy. Both these test were performed under a variation of ionizer powers to examine if any sign of a change in the dominating ionization mechanism could be coupled to the sputter intensity. The energy analysis was done at a low acceleration energy (6 kV) for best energy resolution. In the first test the ionizer power was reduced in steps until the blue light was no longer observable. An expected decrease in total magnitude of the currents was observed, but the ratio $C^- /C_2^-$ remained constant. Neither was any drastic change in the energy spread of the $^{12}C$ peak seen, when going from high to low ionizer power. From figure 4 it can be seen that when the ionizer was lowered from 170 W, where blue light was emitted, to 90 W, where there was no blue light to be seen with the naked eye, the high energy tail of the normalized mass peaks remained constant. No significant low energy tail was detected. A slight broadening of the peak can, however, be associated with the increased ionizer power (and hence also the $^{12}C$ current).

The position of our view port did not allow us to deduce whether the blue light is emerging directly from the sample surface or from a region extending in front of the cathode in the beam direction. However, recent observations made by a member of our group on a different multi-cathode SNICS II source, reveals that blue light can also be seen in a volume around the cathode if the cesium focus is moved so that the $Cs^+$ beam is covering an area surrounding the cathode. The light from this observation has not been analyzed spectroscopically in this study.

## IV. DISCUSSION

From the measured spectra we can confirm the assumption that the blue light often seen in front of the sample in a Middleton cesium sputter source is indeed coming from cesium. In carbon this light originates exclusively from the two persistent lines at 455.528 and 459.317 nm in neutral cesium and a broad peak of unknown origin from 480 to 515 nm. In the two metallic cathodes measured here the main emission in the blue was originating from the 455.528 nm line in neutral Cs and several lines in $Cs^+$. Additionally, there are emission lines at other wavelengths in all three cathodes, mostly from neutral and, in the metallic cathodes case, singly ionized cesium, but also from several alkali metals and the cathode material.

A spectrum of Cs plasma in non-equilibrium between 450 to 525 nm, taken by J. R Cussenot *et al.* [13] is very similar to the spectra retrieved from the aluminum cathode in this wavelength region. The spectral signal from a plasma found in the observed cathode light, strongly suggests that a cesium plasma is really formed in front of the cathode.

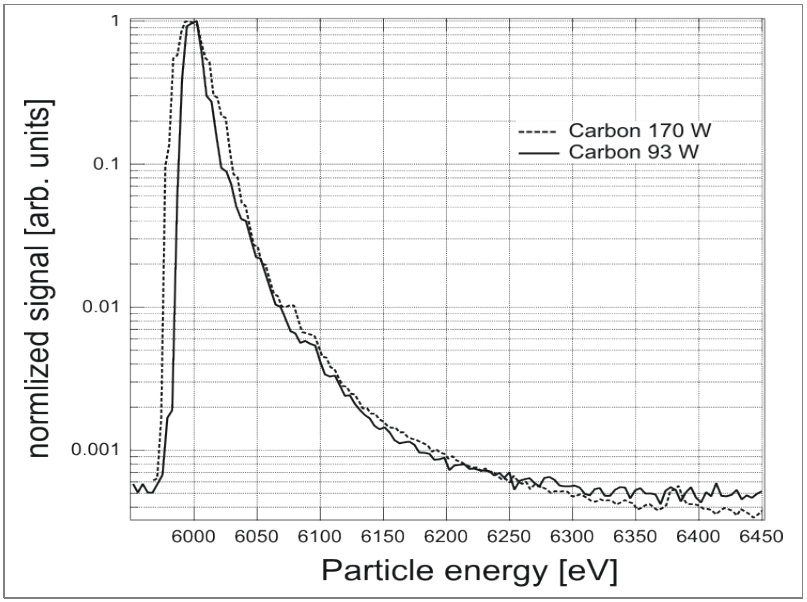


FIG. 4. The high-energy tail on the $^{12}C$ peak for two different ionizer powers. For high ionizer power, i.e. 170 W there is a blue light emitted from the cathode. At low powers i.e. about 90 W, no light whatsoever could be seen. The mass peaks have been normalized for comparison. The current at 170 W was about 100 nA, at 90 W the current was two orders of magnitude smaller.

For carbon, the lack of a low energy tail in the energy analysis and especially the absence of lines from $Cs^+$ in the spectra are not in favor of a cesium plasma being formed in front of the sample. The broad peak in the carbon spectra is unlikely to originate from $Cs^+$. The peaks from the Cs-plasma seen in front of the aluminum cathode fall under the wavelength range of this broad feature but are in contrast well separated. The broad feature is only present when carbon is in the source and its most likely source will have to be a carbon compound. For the moment we do not have any definite candidate for its origin. The blue light emitted from the carbon sample is, according to our result, more likely to be interpreted as neutral cesium, that after being implanted in the sputtering process, is being sputtered out again in an excited state from the carbon surface, rapidly de-excites and emits the blue light observed.

The characteristics of the sputter source output remained the same, whether the blue light was observable or not. There was no change in high energy tail of the observed mass peaks (see fig. 4) and the current ratio of 12C-atom and the 12C-molecule stayed constant. Therefore, in the case of carbon, we see no evidence for different mechanisms of ion formation at high respective low ionizer power, i.e. at a total source output from several tens of μA down to hundreds of nA. Hence is the result from the carbon measurement in strong favor of electron tunneling surface ionization as a dominating ionization mechanisms, while in the two metallic cases, aluminum and copper, the large amount of $Cs^+$ lines are possible indications of a higher degree of post ionization in a cesium plasma.

Better knowledge of the negative ion forming mechanisms could be beneficial for the possibilities of isobar suppression already in the source. In a recently published paper we have demonstrated the change in output from a chlorine cathode when it is radiated with a focused laser light [14]. We could not give a satisfactory explanation for this effect, but changing the population of excited cesium neutrals in a front of the cathode by laser induced excitation and thereby induce a change in the total cross-section for charge transfer have been speculated as a possible cause [11].

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## VI. REFERENCES

[1]T. Andersen, Phys. Rep.-Rev Sect. Phys Lett. **394** (4-5),157-313 (2004)

[2]R. Hemsworth, H. Decamps, J. Graceffa, B. Schunke, M. Tanaka, M. Dremel, A. Tanga, H. P. L. De Esch, F. Geli, J. Milnes, T. Inoue, D. Marcuzzi, P. Sonato, and P. Zaccaria, Nucl. Fusion **4,** 045006(2009)

[3]D. A. Bromley, Nuclear Instruments and Methods **122** 1 (1974)

[4]A. E. Litherland, X-L. Zhao And W. E. Kieser, Mass Spectrometry Reviews, DOI: 10.1002/mas.20311 (2010)

[5]R. Middleton, Nucl. Instr. & Meth.in Phys. Res. 214 (2-3),139(1983)

[6]K. Wittmaack,Ion Beam Science. Solved and Unsolved Problems, Part II 465 (2007)

[7]H. Gnaser, Phys. Rev. B 54 (23) 16456 (1996)

[8]H. Gnaser, *Energy and Angular Distributions*

*of Sputtered Species*. Sputtering by Particle Bombardment, Springer Berlin / Heidelberg (2007)

[9] P.  Philipp, T. Wirtz, H.-N. Migeon, H. Scherrer, Int. J. Mass Spect. **253**, 71 (2006)

[10] G. Doucas, Int. J. Mass Spectrom. Ion Processes  **25** (1) 71 (1977)

[11] J. S.Vogel, J. A. Giacomo, S. R Dueker, Submitted to Nucl. Instr. Meth B ,  Private communication

[12] Middleton R., A *Negative Ion Cookbook*, University of Pennsylvania, USA, 1989 (unpublished) Available (2011) at *www.pelletron.com/**cookbook**.pdf*

[13] J. R.Cussenot, M. Fabry, A.Vicherat, Plasma Phys. **13**, 80 (1971)

[14] M. Martschini,, J. Rohlén, P. Andersson, R. Golser, D. Hanstorp, A. O. Lindahl, A. Priller, P. Steier, O. Forstner, Int. J. Mass Spect. **315 (**1) 55 (2012)

[15] V. Kaufman and W. C. Martin, J. Phys. Chem. Ref. Data **20**, 775 (1991)

[16] C. E. Moore, *Tables of Spectra of Hydrogen, Carbon, Nitrogen, and Oxygen,* J. W. Gallagher, ed., CRC Press, Inc., Boca Raton, FL (1993)

[17] H. Kleiman, J. Opt. Soc. Am. **52**, 441 (1962).

[18] C. J. Sansonetti, Dissertation, Purdue University (1981).

[19] D. C. Morton, Astrophys. J. Suppl. Ser. **149**, 205 (2003).

[20] K. B. Eriksson, I. Johansson, and G. Norlén, Ark. Fys. **28**, 233 (1964)

[21] P. Risberg, Ark. Fys. **10**, 583 (1956).

[22] C. B. Ross, Jr., Ph. D. Dissertation, Purdue Univ. (1969).

[23] A. G. Shenstone, Phil. Trans. R. Soc. (London) **241A**, 297 (1948).

[24] L. J. Radziemski, R. Engleman, Jr., and J. W. Brault, Phys. Rev. A **52**, 4462 (1995).

Appendix 1

Table I,II and III: Identified peaks in the spectrum of aluminum, Carbon filled copper and copper cathodes respectively.

| **Aluminum cathode**: | | | |
|---|---|---|---|
| Peak position (fitting error) [nm] | Normalized strength | emitter | Line position [nm] [Ref.] |
| 396.0(1.0) | 9.00 | Al I | 394.401 + 396.152 [15] |
| 427.0(0.1) | 0.35 | C II | 426.700 + 426.726 [16] |
| 455.71(0.04) | 1.00 | Cs I | 455.528 [13,18] |
| 460.37(0.05) | 0.88 | Cs II | 460.379[13,18] |
| 466.8(0.2) | 0.21 | Al II | 466.306 [15] |
| 483.15(0.12) | 0.19 | Cs II | 483.02 [13,18] |
| 487.2 (0.09) | 0.31 | Cs II | 487.00[13,18] |
| 495.53 (0.08) | 0.34 | Cs II | 495.28 [13,18] |
| 497.37 (0.17) | 0.20 | Cs II | 497.26 [13,18] |
| 504.56 (0.06) | 0.28 | Cs II | 504.38 [13,18] |
| 522.9(0.1) | 0.55 | Cs II | 522.704 [13,18] |
| 556.4(0.1) | 0.31 | Cs II | 556.302 [18] |
| 592.83(0.08) | 0.42 | Cs II | 592.563 [18] |
| 624.5(0.1) | 0.42 | Al II | 624.336 [15] |
| 672.36(0.05) | 0.64 | Cs I/Cs II | 672.328 + 672.447 [18] |
| 766.13(0.17) | 2.45 | K I | 766.49 [19] |
| 769.88( na ) | 1.09 | K I | 769.9 [19] |
| 852.31(0.01) | 59.70 | Cs I | 852.133 [20] |
| 894.57(0.03) | 47.15 | Cs I | 894.345 [20] |

| **Carbon filled copper cathode**: | | | |
|---|---|---|---|
| Peak position (fitting error) [nm] | Normalized strength | Emitter | Line position [nm] [Ref.] |
| 455.71(0.04) | 1 | Cs I | 455.528 [13,18] |
| 459.7(0.1) | 0.23 | Cs I | 459.317 [17] |
| 496.9 (497.3) | n.a. | C related | Broad unknown feature |
| 589.28(1.64) | 0.16 | Na I | 588.995 [21] |
| 601.01 (0.201) | 0.20 | Cs I | 601.049[17] |
| 621.44 (0.07) | 0.31 | Cs I | 621.31[17] |
| 672.35(0.04) | 0.43 | Cs I | 672.328[18] |
| 697.69(0.11) | 0.76 | Cs I | 697.33[17] |
| 723.16(0.21) | 0.5 | C II | 723.132 + 723.642 [16] |
| 766.61(0.03) | 5.58 | Cu I + K I | 766.465 + 766.49 [22,19] |
| 769.91(0.08) | 4.02 | K I | 769.896 [19] |
| 852.16(0.01) | 94.46 | Cs I | 852.113 [20] |
| 894.47(0.01) | 65.65 | Cs I | 894.347 [20] |

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| **Copper cathode**: | | | |
|---|---|---|---|
| Peak position (fitting error) [nm] | Normalized strength | Emitter | Line position [nm] [Ref.] |
| 426.84(0.13) | 0.48 | C II | 426.700 + 426.726 [16] |
| 455.66(0.07) | 1.00 | Cs I | 455.528 [13,18] |
| 460.45(0.05) | 1.31 | Cs II | 460.379[13,18] |
| 522.26(0.07) | 1.87 | Cu I + Cs II | 521.82 + 522.704 [13,18] |
| 556.35(0.11) | 0.75 | Cs II | 556.302 [18] |
| 592.67(0.25) | 0.67 | Cs II | 592.563 [18] |
| 621.56(0.23) | 0.71 | Cs I | 621.31[17] |
| 670.5(2.2) | 1.03 | Li | 670.777 + 670.793 [24] |
| 672.3(3.7) | 1.06 | Cs I + Cs II | 672.328 + 672.447 [18] |
| 697.38(0.018) | 1.73 | Cs I | 697.33[17] |
| 766.54 (0.07) | 9.36 | Cu I + K I | 766.465 + 766.49 [22,19] |
| 769.73(3.5) | 5.65 | K I | 769.896 [19] |
| 852.16(0.01) | 367.11 | Cs I | 852.113 [20] |
| 894.47(0.01) | 309.84 | Cs I | 894.347 [20] |

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