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Use of activated charcoal for the purification of neon in the CLEAN experiment

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Abstract

Passage of neon gas through activated charcoal is planned to be the primary method of removing impurities from the liquid neon scintillator in the CLEAN experiment. In order to quantify this technique, the breakout curves for hydrogen, nitrogen, argon and krypton impurities in neon-saturated activated charcoal were measured. Adsorption coefficients and the number of theoretical stages were measured for hydrogen in the temperature range between 300 and 80 K, nitrogen between 300 and 200 K, and argon between 300 and 190 K. The adsorption coefficient for krypton was measured at 300 K.

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1. Introduction

CLEAN is a detector concept based on the use of 10–100 ton of liquid neon as a scintillator. While the primary focus of CLEAN is a measurement of the p–p solar neutrino flux [1,2], CLEAN will also be able to search for dark matter in the form of weakly interacting massive particles [2,3] and detect supernova neutrinos [4].

There are several characteristics of liquid neon (LNe) that make it an attractive detection medium for rare events. Like other noble liquids, LNe scintillates brightly in the hard UV and does not absorb its own scintillation light. This allows for efficient light collection in a large detector. LNe is dense enough ($\rho = 1.2\,\mathrm{g\,cm^{-3}}$) that a fiducial volume can be defined to mitigate backgrounds from the cryostat and the photomultipler tubes (PMTs). This is more difficult with liquids of significantly lower density than LNe, such as liquid helium. LNe also has both a prompt and a slow scintillation component, thus making it possible to use pulse-shape analysis to distinguish between WIMP-like nuclear recoil events and gamma rays or neutrinos [5].

The use of activated charcoal as an adsorbent for radioactive decay products has been well established. Charcoal traps have been tested in other low-energy detectors such as BOREXINO [6,7] and XENON [8]. Neon presents two distinct purification advantages over other scintillators. Neon has no inherent radioactivity, unlike argon, krypton and xenon which have natural radioactivity from the isotopes ^{39}Ar, ^{85}Kr and ^{136}Xe, and organic scintillators which must contend with the decay of ^{14}C. Neon also has a low binding energy to charcoal compared with possible impurities (see Table 1); only helium has a lower binding energy presenting an opportunity for superior purification [9].

As with other solar neutrino experiments such as BOREXINO, CLEAN requires high purity of its scintillator in order to achieve a low-energy threshold and sufficiently low-radioactive background. In this paper we will present data on the use of cryogenic charcoal traps to remove impurities from neon in the gas phase.

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Table 1
Binding energies (E_b) and well depths (D) of specific atomic species to charcoal [10]

Species	E_b (meV)	D (meV)
^{3}He	11.72 ± 0.1	16.6 ± 0.4
^{4}He	12.35 ± 0.17	15.8
Ne	30.1	32.6
H_2	41.6 ± 0.3	51.7 ± 0.5
Ar	99 ± 4	96 ± 2
N_2	NM	104 ± 3
O_2	NM	101.7
Kr	126	125 ± 5

NM indicates that a quantity was not measured.

1.1. Impurities

Neon contains trace contaminants from two classes: Extreme Ultraviolet (EUV) absorbers (particularly hydrogen, nitrogen, oxygen, water and carbon dioxide) and radioactive impurities (particularly, argon, krypton and radon). EUV absorbers will decrease the number of detected photons from any scattering event by quenching excited Ne_2 molecules or by absorbing the scintillation light. Radioactive impurities can decay creating ionization events indistinguishable from ν–e scattering, the signal for measuring the p–p neutrino flux.

Of the radioactive isotopes, ^{222}Rn can be easily purified through activated charcoal traps [11,12], and any additional radon will decay away within a month of running CLEAN [2] leaving a negligible amount of decaying radon daughters. Both ^{39}Ar and ^{85}Kr are critical contaminants for CLEAN because of their long lifetime and β^- emission in the same range as that of the p–p neutrino flux (0–420 keV). Of these two radioactive isotopes, ^{39}Ar is produced by muon spallation on ^{40}Ar with an atmospheric abundance of $8.1 \pm 0.3 \times 10^{-16}$ [13] and ^{85}Kr is a fission product of ^{235}U and ^{239}Pu with an atmospheric abundance of 1.5×10^{-11} [14].

Detailed Monte Carlo simulations were performed [3] to estimate acceptable levels of contaminants in neon for a measurement of the p–p neutrino flux to the 1% uncertainty level. The acceptable level of natural krypton is the most stringent requirement with a concentration of $\leqslant 10^{-15}$ g g^{-1}. Evaluating such low levels of krypton background is challenging, but a method using atom trap trace analysis (ATTA) is in development [15] and is proceeding along with the other R&D activities of CLEAN. Levels of natural argon must be $\leqslant 10^{-10}$ g g^{-1}. Typical concentrations in commercial neon are 10^{-6} g g^{-1} for argon and $< 10^{-7}$ g g^{-1} for krypton.[1]

To achieve a 95% relative light yield, an absorption length of 300 m is required. By applying known cross-sections for photon absorption at 80 nm [16] the following mass fraction limits were obtained: 2.2, 9.8, 26.8 and 21.6×10^{-12} g g^{-1} for hydrogen, water, nitrogen and oxygen, respectively [17].

2. Removal of impurities using cryo-adsorption

2.1. Background

We define adsorption as the process where molecules (whether neon or impurities) physically bind to the charcoal surface. We only concern ourselves with physical adsorption because it is a reversable process [18]. By heating the charcoal adsorber we can remove any molecules attached to its surface making activated charcoal a reusable purification method. An example breakout curve is presented in Fig. 1. Following a spike impurity in the neon flow, the impurity enters the charcoal trap at $t = 0$ and is adsorbed onto one of the many porous binding sites. The impurity continues through the trap until it breaks out at $t = t_b$. We can relate the flow rate, v, the breakout time, t_b, and the mass of the charcoal absorber, m_{ads}, with the following equation that defines the adsorption coefficient,

$$\alpha = \frac{v t_b}{m_{ads}} \quad (1)$$

where α is measured in 1 kg^{-1}. While the neon carrier gas will also bind to adsorption sites, it will be released relatively quickly compared to impurities because of its much lower binding energy. In the CLEAN experiment, neon gas will flow through a charcoal trap until the shortest breakout time of the impurities of concern is reached. The neon flow will then be diverted to a different charcoal trap while the first trap is baked to remove impurities. This procedure of exchanging traps will continue throughout the experiment to preserve the continuity of the purification process.

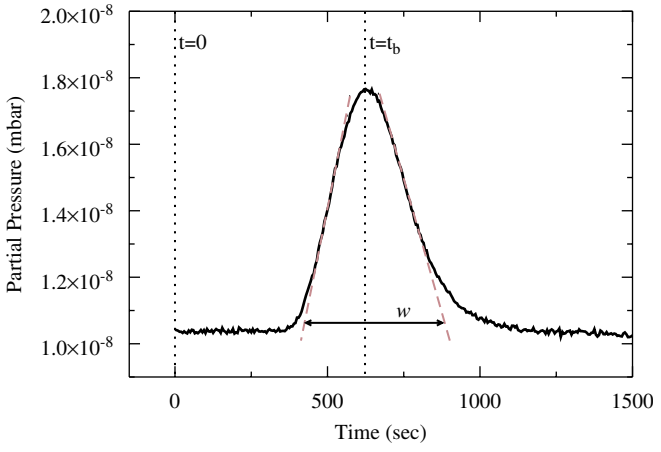

Fig. 1. Breakout curve for H_2 at 120 K with $w = 475$ s (see Eq. (3)) and $t_b = 625$ s.

[1]This krypton concentration is near our detection threshold so it should be considered an upper-bound.

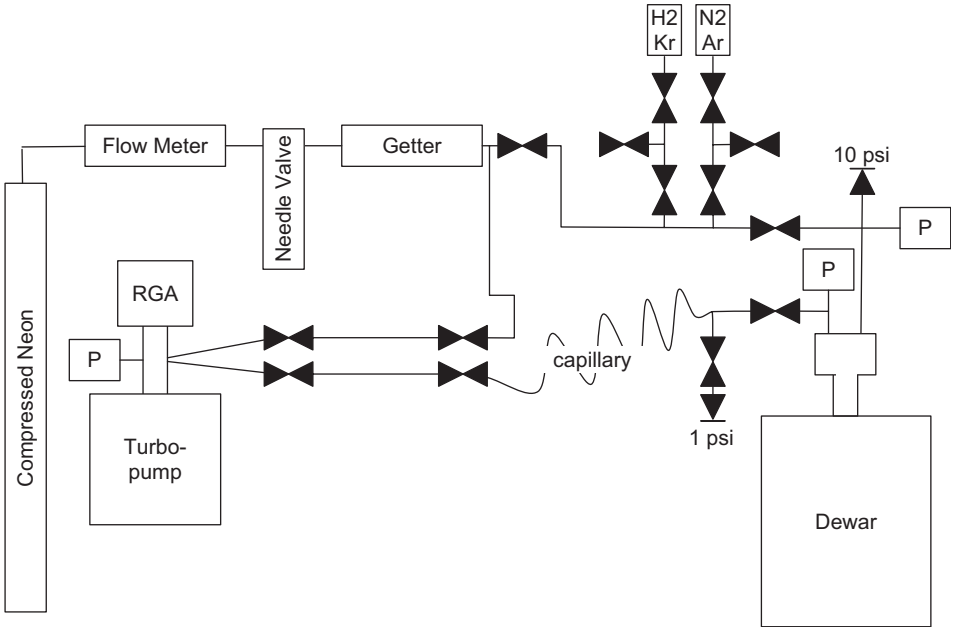

Fig. 2. Gas handling system used to introduce impurities into the Ne flow.

2.2. Experimental procedure

Purification occurs in a neon-saturated trap at constant temperature (T) and pressure (P). We maintain constant T and P by continuously flowing neon through the experimental trap and by not releasing any impurity until the desired temperature has stabilized. Breakout times are measured by introducing 10 ml of impurity into the neon flow in <3 s. The argon, nitrogen, hydrogen and krypton impurities are research grade gas.[2] Using Fig. 2 as a guide, neon gas is released from the bottle and sent though a flow meter and needle valve to control the gas flow. The gas is then pre-purified using a getter before an impurity spike is passed into the flow using the space between two metal valves. The gas mixture then enters the dewar, whose contents are shown in Fig. 3. Neon along with the impurity spike flows into the charcoal trap via a copper heat exchanger attached directly to the first stage of a pulse tube refrigerator (PTR).[3] The heat exchanger is two meters of 1.6 mm ID copper tubing sandwiched between two OFHC copper plates. This heat exchanger is used to pre-cool the gas before it enters the charcoal trap.

The charcoal trap (12.7 cm length and 3.4 cm inner diameter) is attached directly to the second stage of the PTR via a heat link. The trap is filled with approximately 150 g of 203CKrXe 20×100 mesh charcoal.[4] The

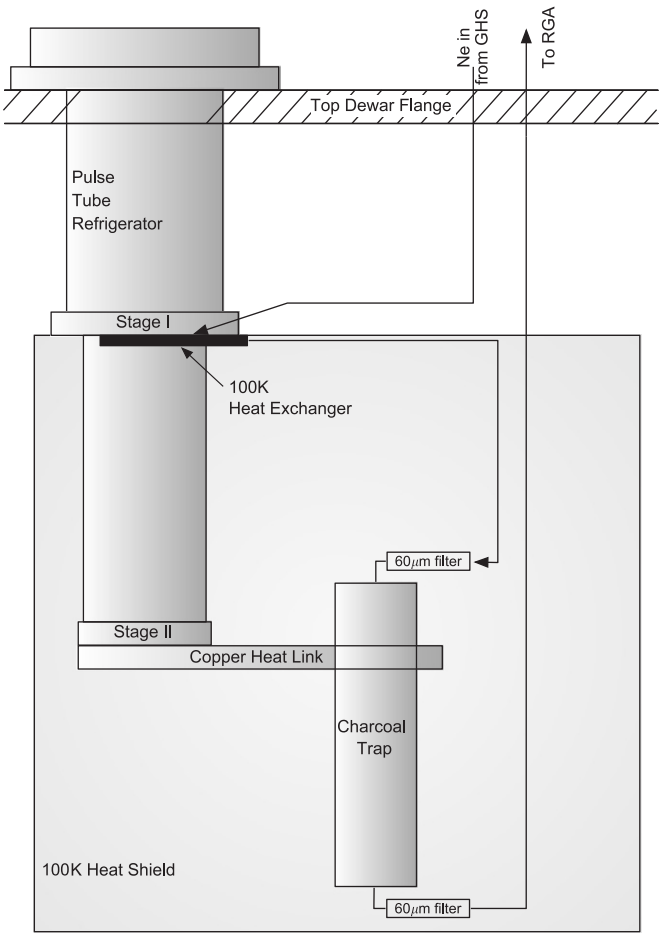

Fig. 3. Charcoal Trap attached to pulse tube refrigerator (PTR) for use in breakout time tests.

[2]⟨http://www.techair.com⟩.

[3]Cryomech Model PT805, ⟨http://www.cryomech.com⟩.

[4]Manufactured by Barnebey and Sutcliffe Corp., ⟨http://www.calgoncarbon.com⟩.

Table 2
Fitting parameters for adsorption coefficients with a scaling factor, α_0 and interaction energy, E_b

Species	α_0 (l kg^{-1})	E_b (meV)
H_2	$3.86 \times 10^{-1} \pm 1.07 \times 10^{-1}$	57.8 ± 2.1
N_2	$1.06 \times 10^{-3} \pm 1.97 \times 10^{-3}$	216 ± 31
Ar	$1.35 \times 10^{-4} \pm 1.01 \times 10^{-4}$	255 ± 13

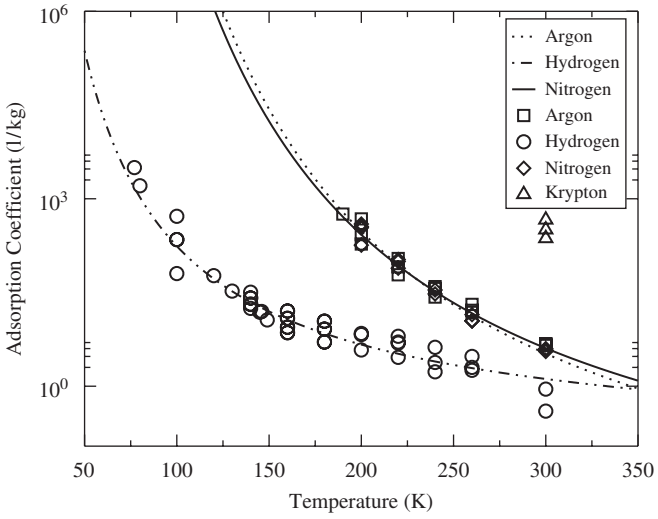

Fig. 4. Calculated adsorption coefficients with curve fits (Eq. (2)) extrapolated to 50 K.

temperature of the trap is measured at two points in order to ensure a uniform temperature across the trap.

Upon exiting the trap the flow is sent from the dewar back into the gas handling system (see Fig. 2) where a small amount of gas is sent through a capillary for monitoring by a residual gas analyzer (RGA), while the rest of the gas is sent to atmosphere through a purge pipe. The RGA[5] continuously monitors the gas flow and records the time since the impurity was introduced as well as the breakout curve. It is sensitive to partial pressures $>10^{-11}$ mbar.

An alternate charcoal trap is used to gather breakout data for krypton because of its much higher adsorption constant. This trap is built from 25 cm of 1.9 mm inner diameter copper tubing and filled with 20 g of charcoal. This trap is also used for hydrogen at 77 K.

2.3. Theory and data

Experimental breakout times were recorded for hydrogen in the temperature range 300–80 K, nitrogen from 300 to 200 K and argon from 300 to 190 K. From these breakout times adsorption coefficients were calculated. Using the alternate 20 g trap breakout times were measured

[5]MKS e-vision with faraday-cup, ⟨http://www.mksinst.com⟩.

Table 3
Calculated values of N for H_2 and N_2 for $v = 1.0$ liters/minute, Ar for $v = 2.0$ liters/minute and Kr for $v = 1.0$ liters/minute

Species	300 K	260 K	240 K	220 K	160 K	140 K	120 K	100 K	77 K[a]
H_2	–	–	–	–	56	31	27	44	46
N_2	81	76	50	44	–	–	–	–	–
Ar	45	31	30	25	–	–	–	–	–
Kr[a]	1	–	–	–	–	–	–	–	–

[a]Indicates data collected using 20 g trap.

for krypton at 300 K and hydrogen at 77 K. Fits to the data were obtained by treating the adsorption coefficient as an exponential dependent on temperature [19–21] and fitting the data to,

$$\alpha = \alpha_0[e^{(-E_b/kT)} - 1]. \quad (2)$$

A table of the fit parameters and a graph of calculated adsorption coefficients with curve fits extrapolated to 50 K are shown in Table 2 and Fig. 4, respectively.

For a high adsorption efficiency, α should be maximized while the width of the breakout curve is minimized. The width of the breakout curve is characterized by the quantity N, which is a measure of the number of theoretical stages for a specific volume and geometry of charcoal [22]. N is calculated by fitting the breakout curves to a Poisson probability distribution and calculating w, the width at the base between tangents to the points of inflection, and $V_{ret} = \alpha m_{ads}$, where

$$N = 16\left(\frac{V_{ret}}{w}\right)^2. \quad (3)$$

While we are able to determine breakout times at low temperature, our calculation of N has a higher-temperature threshold since N requires the entire breakout curve, not just the peak center. Calculated values of N for hydrogen and nitrogen at 1.0 liters/minute, argon at 2.0 liters/minute and krypton at 1.0 liters/minute are presented in Table 3 for temperatures between 300 and 77 K. An example breakout curve is shown in Fig. 1. For $N > 10$ the column is considered not to be dominated by diffusion.

3. Conclusion

In summary, adsorption coefficients were measured for hydrogen, nitrogen, argon and krypton in neon-saturated charcoal. The separation of hydrogen from neon proved quite effective, with N values well above the diffusion limit. Other impurities showed even higher adsorption constants for a given temperature. More work should be done to investigate adsorption properties at lower temperature. This will require greater RGA sensitivity and additional charcoal mass. While the charcoal chosen appears robust, a study of other types of charcoal, including synthetic zeolites, may also prove informative.

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