SCINTILLATOR PURIFICATION BY SILICA GEL CHROMATOGRAPHY IN THE CONTEXT OF LOW COUNTING RATE EXPERIMENTS

L. NIEDERMEIER, C. GRIEB, D. D'ANGELO, G. KORSCHINEK, L. OBERAUER, F. VON FEILITZSCH

Technische Universität München
Boltzmannstrasse
85748 Garching, Germany
E-mail: ludwig.niedermeier@ph.tum.de

Liquid scintillators used in low counting rate experiments – like solar neutrino experiments – usually have to fulfil high requirements concerning their radiopurity. In that context silica gel chromatography is a promising purification method to extract traces of polar impurities out of liquid scintillators. The paper presents a purification model describing two different purification modes and compares it to laboratory experiments performed during the last years. Some of them – large scale purification tests – have been realised at the CTF, prototype of the solar neutrino experiment Borexino.

1. Introduction

Purification with silica gel is a general method to reduce concentrations of polar impurities in organic liquids to ultra low levels. In the context of low counting rate experiments like the solar neutrino experiment Borexino [1] it can contribute to achieve the purity requirements of the liquid scintillator. Small and large scale purification tests were performed, partially also involved CTF [1], a Borexino prototype detector containing 4 tons of liquid scintillator.

2. Theory

2.1. *Static Model*

As the silica gel surface consists of polar OH groups, polar substances prefer to adsorb on it. According to [2] the surface density of adsorption sites amounts to 4.6 nm^{-2}. The porosity of silica gel leads to an outstanding surface to volume ratio in the order of 500m^2/g, resulting in adsorption site densities at about $7 \cdot 10^{21}$ cm^{-3} for
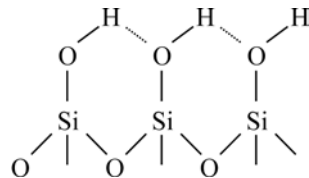

Fig. 1: Silica gel surface

solid silica gel and 10^{21} cm^{-3} for silica gel powder.

In contact with air silica gel adsorbs water molecules, which can be removed by heating it to 150-200°C for several hours (conditioning).

A quantitative examination of the purification process – organic liquid being in contact with silica gel – can be derived by assuming an equilibrium between dissolved impurities in the liquid and adsorbed ones on the silica gel surface. Thus an equilibrium constant $k = c\ (Y\ in\ S) \cdot c\ (L)\ /\ c\ (Y\ in\ L) \cdot c\ (L\ in\ S)$ gives the ratio between the impurity (Y) concentration in the silica gel (S) and the impurity concentration in the liquid (L), whereby c (L) / c (L in S) can be calculated with respect to the liquid density and the adsorption site density.

The equation $\Delta G = -\ R\ T\ ln(k)$ is relating k to the free enthalpy ΔG in dependence of the temperature T and the gas constant R. Note that ΔG is a natural constant depending on solvent, silica gel and impurity type, whereas k varies at different temperatures.

This model describes a static situation of a thermodynamic equilibrium in a silica gel volume. To comprehend a purification process including liquid flow through a silica gel column (Fig. 2) it has to be expanded.

2.2. *Dynamic Model*

The essential step consists in the definition of a time constant τ necessary to reach an equilibrium between the impurities in the liquid and on the silica gel surface.

Depending on the flow velocity v of the liquid, the latter is covering the distance x during the time τ. The total column height h divided by x leads to the number of so-called *segments*, telling how many different equilibrium states the liquid can reach in the silica gel. Considering each single equilibrium as static after the time span τ, the whole process can be simulated by applying the ΔG-equation in each *segment* and relating them subsequently.

Fig. 2

During purification the impurity concentration in the silica gel is forming a gradient along the column height with increasing purity towards the exit. This gradient is particularly high in a limited number of column segments and therefore forms a contamination front that moves through the column. The moment when this front reaches the final column segment and hence comparatively high contamination (dark coloured in Fig. 2) begins to exit the column is called *breakthrough*.
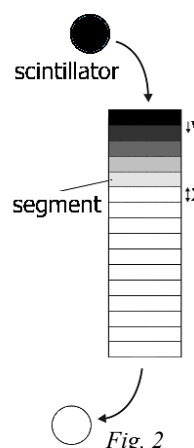
2.3. *Loop mode and Batch mode*

The described model has been applied on two different purification modes. During the so-called *batch purification* the purified liquid is collected in a separate, necessarily ultra pure vessel. During the *loop purification*, on the contrary, the liquid is circulated between the purification column and only one vessel, thus implying a continuous mixing of purified and unpurified liquid.

In batch mode, the expected purification factor is by far higher as long as the *breakthrough* point is not reached. From that point on comparatively high contaminated scintillator would exit from the column.

In loop mode processes the impurity concentration in the liquid vessel first is decreasing slowly and continuously until the *breakthrough*. Then, however, it starts to settle in a damped oscillation around the thermodynamic equilibrium described by the static ΔG-equation (see Fig. 3).

3. Purification Measurements

3.1. *Small Scale Tests in Laboratory*

Liquid scintillator (pseudocumene + 1.5 g/l of PPO) was activated by a Rn emanating ^{226}Ra source with its daughters ^{210}Pb, ^{210}Bi and ^{210}Po – actually these isotopes are causing the major background in CTF [3] and Kamland [4]. Then the scintillator (39.0 g each time) was purified by a 3.0 g silica gel column at about 300 K. The gel was contained in a glass syringe with a nylon filter at the outlet. The activity in the scintillator was measured before and after the purification step in a small teflon vessel connected by a glass window to a photomultiplier (Ø 7 cm). See the results in Table 1.

Table 1: Small scale purification results

Silica gel type (company, pore size, grain size)	^{210}Po purification		^{210}Bi purification	
	final concentr.	pur. factor	final concentr.	pur. factor
Merck, 60Å, 64-200µm	$(8.0\pm1.0)10^{-18}$	350^{+90}_{-80}	$(7.2\pm2.0)10^{-18}$	24^{+16}_{-9}
Merck, 60Å, 64-200µm	$(1.21\pm0.15)10^{-17}$	400^{+70}_{-50}	$(6.6\pm0.6)10^{-18}$	53^{+7}_{-6}
Eka Nobel, 60Å, Ø16µm	$(9.3\pm2.3)10^{-18}$	520^{+200}_{-110}	$(2.7\pm1.1)10^{-18}$	130^{+90}_{-40}

As the silica gel mixed up with the whole scintillator batch each time the latter was put into the syringe, it is to assume that one single equilibrium state

(segment) formed in the whole column. The situation can be described with the static ΔG-equation, leading to free enthalpy values of –23±1 kJ/mol concerning Po and −18±2 kJ/mol concerning Bi. Due to the exposure time between scintillator and silica gel, the time constant τ could be confirmed to be less than 100s. To condition the silica gel before purification did not result in a significant difference.

3.2. *Large Scale Tests at Borexino*

Large scale purification tests at the CTF commenced in 1997 (see [5], [6]). Recently a loop mode test was performed with a new silica gel type (Eka Nobel, 2.4 kg) and pseudocumene scintillator (3800 kg). The scintillator of the CTF detector was circulated six times its volume through the silica gel contained in a stainless steel column between a nylon and a teflon filter. CTF took online data during the test. Mainly α-events – the major part of them supposed to be ^{210}Po contamination – were detected and reduced continuously until a final factor of about 2, corresponding to 800 events/day between 250-800 keV. This is mostly confirming the model curve (Fig. 3), after adjustment of some parameters. Moreover, measurements of delayed Bi-Po-coincidences indicated a reduction of ^{238}U and ^{232}Th daughters by factors of 2.0 and 2.5 to concentrations of $(7.6±1.7)10^{-16}$ (^{238}U equivalent) and $(2.1±0.8)10^{-15}$ (^{232}Th equivalent).

Fig. 3: Loop test result; CTF data points compared to theory curve. ^{210}Po concentr. [g/g] above total scintillator flow [m^3].

In addition, a batch purification test at CTF is intended in order to complete the confirmation of the theory model.

4. Radon Emanation

Silica gel contains traces of radioactive elements, among others ^{226}Ra, emanating ^{222}Rn. Due to its mobility as noble gas, latter diffuses quickly into the scintillator and causes background events in the detector.

Table 2 shows Rn emanation measurements of silica gel types and their results, referring to activities at emanation equilibrium. Stainless steel columns usually contribute to the emanation rate in the range of mBq.
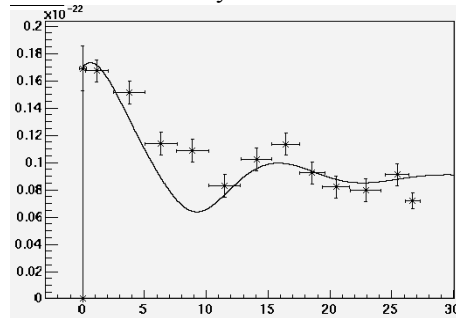
Table 2: ^{222}Rn emanation measurements

Examined object	Emanation rate
15 kg of silica gel (Merck, 60Å, 63-200μm) in stainless steel column, tested 1997 with CTF	172±21 mBq/kg [7]
Silica gel (Merck, 60Å, 64-200μm), measured 1998	200±10 mBq/kg [7]
2.4 kg of silica gel (Eka Nobel, 60Å, Ø10μm) in stainless steel column while CTF loop test in 2002	1.9±0.3 mBq
30 kg of silica gel (Eka Nobel, 60Å, 10-20μm) in st. steel col.	4±2 mBq [8]
Silica gel (Eka Nobel, 60Å, 10-20μm), measured 2002	0.13±0.07 mBq/kg [8]

5. Conclusion

The purification capability of silica gel has been shown at ultra low levels down to U and Th equivalences of 10^{-15} g/g with Bi-Po-coincidences in CTF, further to concentrations of 10^{-18} concerning Bi and 10^{-23} concerning Po in laboratory tests. Positive results have been reached on small and large scales, the CTF loop test confirmed parts of the purification theory model.

Nevertheless, the experimental confirmation of the batch purification is of great importance due to the expected large purification factor. It is intended to perform a batch test either at small scales in laboratory or with the CTF detector.

The silica gel purification plant on Borexino site seems to be set up properly in terms of radiopurity as Radon emanation measurements of both the stainless steel columns and the 'Eka Nobel' silica gel have shown.

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