

## Passing in review of radio-noble-gas measurements by low level counting at University of Bern

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During decades low level counting (LLC) was the only method to detect radioisotopes of argon and krypton at an atmospheric level. Hans Oeschger and Heinz Hugo Loosli pioneered the methodology and application of  $^{85}\text{Kr}$  and  $^{37,39}\text{Ar}$  for environmental research. They determined also the first time the  $^{81}\text{Kr}$ -activity in the atmosphere on a sample of about 5 l of pre-bomb krypton (Loosli et al., 1969). The main challenges of LLC of radio noble gases lay in the low activity concentrations in the hydro- and atmosphere what can only be overcome by larger sample volumes and the effective suppression of background activity in the counting arrangement (Loosli et al, 1986). In Bern the measurements are therefore performed in actively shielded proportional counters in a specially designed underground laboratory (Loosli, et al, 1986). In hydrological applications large volume sampling becomes a crucial and sometimes also a limiting issue (IAEA, 2012, in press). In the past the required volume of water that has to be degassed in the field for  $^{39}\text{Ar}$  or more recently for  $^{85}\text{Kr}$  and  $^{81}\text{Kr}$  analyses decreased steadily. First low level counting  $^{39}\text{Ar}$  measurements in groundwater required about 10 tons of water to be processed in the field (LOOSLI, 1983; LOOSLI et al., 2000). In the first  $^{81}\text{Kr}$  study in the Great Artesian Basin (GAB) in Australia, measured by AMS (COLLON et al., 2000; LEHMANN et al., 2003), 0.5 cc Kr were collected at each site. This corresponds to a volume of about 17 tons of water. With the improvements of the existing analytical facilities here in Bern and the development of novel techniques (COLLON et al., 2004; DU et al., 2003; JIANG et al., in press) the sample volumes decreased and are expected to decrease further in the future. LLC  $^{39}\text{Ar}$  sample volumes are today typically in the range of 1-2 tons of water whereas for LLC- $^{85}\text{Kr}$  and Atom Trap Trace Analyses (ATTA)  $^{85,81}\text{Kr}$  detection not much more than 100 litres of water are needed. Accordingly, the methods and tools for gas extraction in the field evolved. The classical vacuum extraction (PURTSCHERT, 2008; SMETHIE JR. and MATHIEU, 1986) is often replaced, or at least completed, by commercially available membrane degassing units (OHTA et al., 2009). However, the requirements of a robust and simple sampling procedure, high extraction efficiency and the absence of any contamination with atmospheric air remained the same. While this is relatively simple to achieve in standard situations, i.e. tapped wells or open boreholes with submersible pumps, it becomes more difficult in more exotic environments (STURCHIO et al., 2004).

Similarly, the noble gas purification facilities had continuously to be adjusted to the rapid development of new detection methods (RIEDMANN, 2011). Currently 5-10  $\mu\text{l}$  of Kr are required for a  $^{81,85}\text{Kr}$  ATTA analysis (JIANG et al., in press), a similar amount than for  $^{85}\text{Kr}$  LLC measurements (ALTHAUS et al., 2009). Conventionally, gaschromatographic methods are at least part of each large volume noble gas purification facility (LOOSLI and PURTSCHERT, 2005; MOMOSHIMA et al., 2010). This may be combined or completed by cryogenic distillation (YOKOCHI et al., 2008). In the future, with further decreasing sample volumes, noble gas purification by getter techniques will become more important. However, the parallel purification and detection of Kr and Ar isotopes from the same sample requires an accordingly adapted procedure (LOOSLI et al., 1986; RIEDMANN, 2011).

In the talk a historical review is given about the development and improvements of the methodology of radio-noble-gas measurements at Climate and Environmental Physics Institute in Bern. This includes sampling strategies at different locations world-wide, the adaption of sample processing in connection e.g to  $^{37}\text{Ar}$  measurement in soil air (Riedmann et al., 2011) and the activity measurement

our the underground laboratory. The lesson learned should be a starting point for the discussion of future perspectives.

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