

## **Development of a Coupled Diffusion Denuder System Combined with GC–MS for the Separation and Quantification of Molecular Iodine and Activated Iodine Compounds (ICI, HOI) in the Marine Atmosphere**

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This study concerns the development of a coupled diffusion denuder system capable of separating and quantifying gaseous molecular iodine ( $I_2$ ) and two other highly reactive iodine species, ICI and HOI, which are collectively named activated iodine compounds (AIC). Both  $I_2$  and AIC are key species in the atmospheric chemistry of iodine. 1,3,5-trimethoxybenzene (1,3,5-TMB) and  $\alpha$ -cyclodextrin/ $^{129}I^-$  ( $\alpha$ -CD/ $^{129}I^-$ ) coated denuders proved to be suitable for the collection of gaseous AIC and  $I_2$ , respectively. The experimental collection efficiencies for AIC (tested as ICI) and  $I_2$  agreed well with the theoretical values for gas flow rates in the range between 300 and 1800 mL  $min^{-1}$ . The coupled denuder system (1,3,5-TMB-coated denuder as front-denuder coupled upstream of an  $\alpha$ -CD/ $^{129}I^-$ -coated denuder) was applied successfully to separate test gas mixtures of ICI and  $I_2$  at various mixing ratios in the laboratory. The operation of both denuder systems was demonstrated to be independent of relative humidity (0–100%) and storage period (at least 2 weeks prior to and after sampling). Detection limits were achieved at sub parts-per-trillion-by-volume (sub-pptv) level. The presented method provides a reliable and practical approach for the speciation of gaseous iodine compounds. In addition, we report for the first time ambient air measurements of AIC mixing ratios, carried out at the atmospheric research station in Mace Head, Ireland. A maximum concentration of AIC of 30.2 pptv was observed for nighttime measurements and 6.0 pptv for daytime measurements. A similar diurnal pattern was found for  $I_2$  with an average concentration level of 23.2 pptv during daytime and 85.1 pptv during nighttime, indicating a strong correlation with AIC.