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Supplement of

A versatile, refrigerant- and cryogen-free cryofocusing–thermodesorption unit for preconcentration of traces gases in air

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Supplementary Information

Table S-1 shows a list of substances detected up to the time of completion of this paper. Identifications based on ambient air samples as well as synthetic mixtures. Substances are separated into six classes (e.g. CFCs and HCFCs, PFCs and HFCs etc.), which are listed in arbitrary order. Within each class, substances are sorted according to their boiling point (bp) in [°C]. Chemical sum formula as well as retention time \( t_R \) in [min] on the GS GasPro PLOT column listed in columns two and three. Columns 5 & 6 show analyte residues in [%], expressed as chromatographic signal area determined in a blank gas measurement relative to a signal area determined in a preceding 1 L ambient air sample. Blank gas: purified helium 6.0 (Praxair, Germany). “Residue HayeSep D” denotes residues found with HayeSep D as adsorptive material, “Residue Unibeads 1S” shows the same for Unibeads 1S as adsorptive material. Residues that a constant background (contamination), are marked with a “c”, ones that represent a memory effect from a preceding sample are marked with an “m”. Substances that are not detected regularly in ambient air samples or show poor measurement precision \( \geq 10 \% \) were excluded from the analysis (“not analysed”; n.a.). If no residue was detected or the detected residue was \( \leq 0.01 \% \), a “not detected” (n.d.) is assigned to the respective substance.

Table S-1. List of detectable substances and blank residues. Descriptions are given in the text.

| Class/Name | Formula | \( t_R \) [min] | bp [°C] | Residue HayeSep D | Residue Unibeads 1S |
|------------|---------|-----------------|--------|------------------|-------------------|
| **CFCs & HCFCs** |         |                 |        |                  |                   |
| HCFC-22    | CHClF₂  | 5.20            | -41    | n.d.             | n.d.              |
| CFC-115    | CCl₂F₂CF₃ | 4.48           | -39    | n.d.             | n.d.              |
| CFC-12     | CF₂Cl₂  | 5.02            | -30    | n.d.             | n.d.              |
| HCFC-124   | CHF₂CF₂Cl | 6.85           | -12    | n.d.             | n.d.              |
| HCFC-142b  | CH₃CClF₂ | 6.87            | -10    | n.d.             | n.d.              |
| HCFC-31    | CH₂ClF  | 6.40            | -9     | n.a.             | n.a.              |
| CFC-114    | CCl₂F₂CCl₂F | 6.67       | 4      | n.d.             | n.d.              |
| HCFC-133a  | C₂H₃ClF₃ | 7.55            | 6      | n.d.             | n.d.              |
| HCFC-21    | CHFCl₂  | 7.32            | 9      | n.d.             | n.d.              |
| CFC-11     | CFCI₃   | 7.28            | 24     | n.d.             | n.d.              |
| HCFC-141b  | CH₃CCl₂F | 8.42            | 32     | n.d.             | n.d.              |
| HCFC-1121  | CHClCFCI | 8.05            | 35     | n.a.             | n.a.              |
| Class/Name | Formula | $t_b$ [min] | bp [°C] | Residue HayeSep D | Residue Unibeads 1S |
|------------|---------|------------|---------|------------------|-------------------|
| HCFC-132b  | CH₂ClCCIF₂ | 9.08       | 46      | n.d.             | n.d.              |
| CFC-113    | CCl₃FCCIF₂ | 8.45       | 48      | 0.2% (m)        | n.d.              |
| HCFC-225ca | CF₃CF₂CHCl₂ | 9.37       | 51      | n.a.            | n.a.              |
| HCFC-225cb | CClF₂CF₂CHClF | 9.57     | 56      | n.a.            | n.a.              |
| CFC-112    | CFCl₃CFCl₂ | 10.33      | 92      | n.d.            | n.d.              |
| HCFC-131   | CCl₃CH₂F  | 12.38      | 103     | n.a.            | n.a.              |

**PFCs & HFCs**

|        |        |            |         |                 |                   |
|--------|--------|------------|---------|------------------|-------------------|
| HFC-23 | CHF₃   | 3.01       | -82     | 2.6% (c)        | n.a.              |
| HFC-41 | CH₄F   | 4.38       | -78     | n.a.            | n.a.              |
| HFC-32 | CH₂F₂  | 4.20       | -52     | n.d.            | n.d.              |
| HFC-125| CHF₂CF₃ | 4.87      | -49     | 0.4% (c)        | 1.3% (c)          |
| HFC-143a| CH₃CF₃ | 5.00       | -48     | n.d.            | n.d.              |
| HFC-161 | C₂H₃F  | 6.85       | -38     | n.a.            | n.a.              |
| PFC-218 | C₃F₈   | 4.02       | -37     | n.d.            | n.d.              |
| PFC-216 | C₄F₆   | 4.58       | -30     | n.a.            | n.a.              |
| HFO-1234yf | CHFCHCF₃ | 5.72    | -28     | 6.9% (c)        | 14.9% (c)         |
| HFC-134a | CH₂FCF₃ | 5.92       | -26     | n.d.            | n.d.              |
| HFC-152a | CH₃CHF₂ | 6.53       | -25     | n.d.            | n.d.              |
| HFC-134 | CHF₂CHF₂ | 6.32      | -23     | 1.1% (c)        | 3.0% (c)          |
| HFC-227ea | CF₃CHFCF₃ | 6.52    | -16     | n.d.            | n.d.              |
| HFO-1234ze | CHFCHCF₃ | 6.27      | -16     | n.d.            | n.d.              |
| PFC-318 | c-C₄F₈ | 5.68       | -6      | n.d.            | n.d.              |
| HFC-236fa | CF₃CH₂CF₃ | 7.22      | -1      | n.d.            | n.d.              |
| HFC-329ccbb | C₄HF₉ | 7.67       | 15      | n.a.            | n.a.              |
| HFC-245fa | CF₃CH₂CHF₂ | 7.92     | 15      | n.d.            | n.d.              |
| HFO-1233zd | CHClCHCF₃ | 7.82     | 19      | n.a.            | n.a.              |
| HFC-356mff | C₄H₄F₆ | 8.35       | 25      | n.a.            | n.a.              |
| HFC-365mfc | CF₃CH₂CF₂CH₃ | 9.27   | 40      | n.a.            | n.a.              |

**Halons**

|        |        |            |         |                 |                   |
|--------|--------|------------|---------|------------------|-------------------|
| Halon-1301 | CBrF₃   | 3.87       | -58     | n.d.            | n.d.              |
| Halon-1211 | CBrClF₂ | 6.32       | -4      | n.d.            | n.d.              |
| Halon-1202 | CF₂Br₂  | 7.45       | 23      | n.a.            | n.a.              |
| Halon-2402 | CBr₂CBrF₂ | 8.53    | 47      | n.d.            | n.d.              |
| Halon-2311 | CF₃CHBrCl | 9.30      | 50      | n.a.            | n.a.              |
| Class/Name                          | Formula      | $t_r$ [min] | bp [°C]  | Residue HayeSep D | Residue Unibeads 1S |
|-----------------------------------|--------------|------------|----------|-------------------|---------------------|
| **Chloro-, Bromo- & Iodocarbons** |              |            |          |                   |                     |
| Chloromethane                     | CH₃Cl        | 6.02       | -24      | 0.5% (c)          | 0.6% (c)            |
| Bromomethane                      | CH₃Br        | 7.00       | 4        | 3.4% (c)          | 1.8% (c)            |
| Chloroethane                      | C₂H₅Cl       | 7.92       | 12       | 25.5% (c)         | 8.6% (c)            |
| Dichloromethane                   | CH₂Cl₂       | 8.17       | 40       | 0.4% (c, m)       | 0.2% (c)            |
| Iodomethane                       | CH₃I         | 8.00       | 42       | 43.9% (c, m)      | 46.2% (c, m)        |
| Trichloromethane                  | CHCl₃        | 8.92       | 61       | 1.4% (c, m)       | 0.7% (c, m)         |
| Bromochloromethane                | CH₂BrCl      | 9.03       | 68       | n.d.              | n.d.                |
| Methyl chloroform                 | CH₃CCl₃      | 9.93       | 74       | n.d.              | n.d.                |
| Tetrachloromethane                | CCl₄         | 9.08       | 77       | 1.1% (m)          | n.d.                |
| Trichloroethene                   | C₂HCl₃       | 9.55       | 87       | n.d.              | n.d.                |
| Bromodichloromethane              | CHBrCl₂      | 10.10      | 90       | n.d.              | n.d.                |
| Dibromomethane                    | CH₂Br₂       | 10.03      | 96       | n.d.              | n.d.                |
| Dibromochloromethane              | CHBr₂Cl      | 11.53      | 119      | n.d.              | n.d.                |
| Tetrachloroethene                 | C₂Cl₄        | 10.62      | 121      | 23.9% (c, m)      | 5.2% (c, m)         |
| Tribromomethane                   | CHBr₃        | 13.50      | 147      | 11.2% (m)         | n.d.                |
| Diiodomethane                     | CH₂I₂        | 15.00      | 181      | n.a.              | n.a.                |
| **Sulfur-containing and other halogenated compounds** |              |            |          |                   |                     |
| Sulfuryldifluoride                | SO₂F₂        | 4.20       | -55      | n.d.              | n.d.                |
| Carbonyl sulfide                  | COS          | 3.77       | -50      | 0.4% (c)          | 0.1% (c)            |
| Chlorotrifluoroethylene           | C₂F₅Cl       | 4.92       | -28      | n.a.              | n.a.                |
| Perfluorotetrahydrofuran          | C₄F₈O        | 5.87       | 2        | n.a.              | n.a.                |
| 3-chloropentafluoropropene        | CF₂CFCF₂Cl   | 8.07       | 8        | n.d.              | 7.6% (c)            |
| Desflurane                        | CF₃CHFOCHF₂   | 8.42       | 24       | n.a.              | n.a.                |
| Carbon disulfide                  | CS₂          | 6.54       | 46       | 4.0% (c)          | 0.8% (c)            |
| Isoflurane                        | CHF₂OCHCICF₃ | 9.83       | 49       | n.a.              | n.a.                |
| Sevoflurane                       | CF₃CF₃CHOCH₂F | 10.35      | 59       | n.a.              | n.a.                |
| Class/Name     | Formula | $t_r$ [min] | bp [°C] | Residue | Residue |
|---------------|---------|------------|---------|---------|---------|
|               |         |            |         | HayeSep D | Unibeads 1S |
| **Hydrocarbons and Aldehydes** |         |            |         |         |         |
| Ethyne        | C$_2$H$_2$ | 3.75       | 81      | 0.3% (c) | 1.4% (c) |
| Propene       | C$_3$H$_6$ | 5.38       | 48      | 35.2% (c) | 28.5% (c) |
| Propane       | C$_3$H$_8$ | 4.09       | 42      | 0.4% (c) | 0.1% (c) |
| Propyne       | C$_3$H$_4$ | 7.17       | 23      | n.d.     | n.d.     |
| Formaldehyde  | CH$_2$O  | 7.62       | -19     | n.a.     | n.a.     |
| Isobutane     | C$_4$H$_{10}$ | 5.79 | -13 | 0.7% (c) | 1.0% (c) |
| Isobutene     | C$_4$H$_8$  | 7.32       | -7      | n.d.     | 75.3% (c) |
| 1-butene      | C$_4$H$_8$  | 7.38       | -6      | n.a.     | n.a.     |
| 1,3-butadiene | C$_4$H$_6$  | 7.32       | -4      | n.a.     | n.a.     |
| n-butane      | C$_4$H$_{10}$ | 6.05 | -1   | 0.3% (c) | 0.1% (c) |
| trans-2-butene| C$_4$H$_8$  | 7.02       | 1       | 25.3% (c) | 19.8% (c) |
| cis-2-butene  | C$_4$H$_8$  | 7.24       | 4       | n.a.     | n.a.     |
| Acetaldehyde  | C$_2$H$_4$O | 11.26 | 20 | 99.2% (c, m) | 82.0% (c, m) |
| 2-methylbutane| C$_5$H$_{10}$ | 7.40 | 28 | 0.4% (m) | 0.2% (m) |
| Isoprene      | C$_5$H$_8$  | 8.67       | 34      | n.a.     | n.a.     |
| n-pentane     | C$_5$H$_{12}$ | 7.57 | 36 | 0.7% (m) | 0.3% (m) |
| trans-2-pentene| C$_5$H$_{10}$ | 8.47 | 36 | n.d.     | 22.2% (c, m) |
| cis-2-pentene | C$_5$H$_{10}$ | 8.56 | 37 | n.a.     | n.a.     |
| 2-methylpentane| C$_6$H$_{14}$ | 8.61 | 60 | 0.8% (m) | 1.0% (m) |
| 3-methylpentane| C$_6$H$_{14}$ | 8.71 | 63 | 1.8% (m) | n.d.     |
| n-hexane      | C$_6$H$_{14}$ | 8.71 | 68 | 1.5% (c) | n.d.     |
| Benzene       | C$_6$H$_6$  | 11.00      | 80      | 2.5% (c) | 5.2% (c) |
| Cyclohexane   | c-C$_6$H$_{12}$ | 8.82 | 81 | n.d.     | n.d.     |
| n-heptane     | C$_7$H$_{16}$ | 10.06 | 98 | 23.1% (c, m) | 4.0% (m) |
| Toluene       | C$_7$H$_8$  | 14.52      | 111     | 17.4% (c, m) | 9.8% (c, m) |