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Field portable low temperature porous layer open tubular cryoadsorption headspace sampling and analysis part I: Instrumentation☆

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ABSTRACT

Building on the successful application in the laboratory of PLOT-cryoadsorption as a means of collecting vapor (or headspace) samples for chromatographic analysis, in this paper a field portable apparatus is introduced. This device fits inside of a briefcase (aluminum tool carrier), and can be easily transported by vehicle or by air. The portable apparatus functions entirely on compressed air, making it suitable for use in locations lacking electrical power, and for use in flammable and explosive environments. The apparatus consists of four aspects: a field capable PLOT-capillary platform, the supporting equipment platform, the service interface between the PLOT-capillary and the supporting equipment, and the necessary peripherals. Vapor sampling can be done with either a hand piece (containing the PLOT capillary) or with a custom fabricated standoff module. Both the hand piece and the standoff module can be heated and cooled to facilitate vapor collection and subsequent vapor sample removal. The service interface between the support platform and the sampling units makes use of a unique counter current approach that minimizes loss of cooling and heating due to heat transfer with the surroundings (recuperative thermostatting). Several types of PLOT-capillary elements and sampling probes are described in this report. Applications to a variety of samples relevant to forensic and environmental analysis are discussed in a companion paper.

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1. Introduction

In previous work, dynamic headspace vapor collection on short (0.2–3 m), porous layer open tubular (PLOT) capillary columns maintained at low temperature was introduced for chromatographic analysis [1]. This approach has been called PLOT-cryoadsorption, or PLOT-cryo, and can operate either with an applied positive pressure (that is, a sweep gas) or with negative pressure (suction). The method has proven to be sensitive and quantitative, with a sampling limit of detection below 1 ppb (mass/mass) of a test solute (2,4,6-trinitrotoluene, TNT) in the analyte matrix, and it can provide results that are of low enough uncertainty to permit thermodynamic interpretation (by way of the equilibrium constant and associated enthalpy) of recovered concentrations through the van't Hoff equation. With PLOT-cryo, the sample is typically recovered in a solvent for presentation to any analytical instrument such as gas chromatography (with mass spectrometry or other detector, GC–MS), Fourier Transform infrared spectrophotometry (FTIR), nuclear magnetic resonance spectrometry (NMR), ion mobility spectrometry (IMS), etc. [2,3]. This approach to headspace sampling has other important advantages in addition to sensitivity. The low temperature that is used to improve efficiency and facilitate collection is generated with a vortex tube, a device that operates only from a source of compressed air and has no moving parts [4–9]. This aspect in particular makes the approach attractive for locations that lack electrical power and also for environments with explosive or flammable materials [10]. When used in the laboratory, the same vortex tube that is used to generate the low temperature air stream (which can be as low as −40 °C) can also be used to generate a high temperature stream of air (the temperature of which can be as high as 160 °C) to thermally desorb solutes from the PLOT capillary (or to assist the solvent desorption with more gentle heating). The capillaries that are used are robust and inexpensive, and unlike other headspace collection methods, PLOT-cryo is

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especially applicable for relatively involatile solutes because it has a large temperature operability range. Moreover, it is not limited to aqueous samples, as are some commercial headspace instruments. It has been used as an alternative to conventional purge and trap (static and dynamic), [11–18] and even such modern techniques such as SPME [1–20]. Unlike SPME, PLOT-cryo has been shown to be quantitative. A particularly attractive feature of PLOT-cryo is the ability to simultaneously sample a single headspace with multiple, different sorbent phases (selected for their specific functionalities). This has included the clay and organoclay phases developed at NIST that are especially applicable for aromatic and sulfur compounds [21–24]. We have in fact used up to eight separate phases, simultaneously, to collect vapor from the headspace of a single sample. Alternatively, the approach allows sampling multiple samples with multiple PLOT capillaries of the same phase, for repeatability and quality assurance. For example, in recent work, eight vapor samples from eight separate samples of arson fire debris were routinely collected simultaneously in eight separate PLOT capillaries [25]. Moreover, for residual fuel recovered from fire debris, the composition profiles are consistent with predictions made from composition explicit distillation curve measurements [26,27]. This demonstration of consistency with phase equilibrium and the van't Hoff equation is not possible with other headspace collection methods. The method also offers the ability to bundle many PLOT capillaries into a high capacity module that can be used with flow rates similar to those used in packed gas chromatographic columns. These numerous features have been demonstrated with applications to explosives, food safety, arson fire debris analysis and cadaver detection [1,25,28–32].

While PLOT-cryo has performed admirably in the laboratory, there is great motivation for taking the technique out of the lab and into the field; in this paper (Part I) we introduce an adaptation of PLOT-cryo that can be used for sampling outside the laboratory [33]. Applications for this device in criminalistics, food safety and in environmental assessment and enforcement are especially attractive. A companion paper (Part II) presents examples of some of these applications [34].

There are four primary aspects to making the approach functional in the field: (1) the design and construction of a portable PLOT-capillary platform, (2) the design and construction of an appropriate supporting equipment platform, (3) the design of the service interface between the PLOT-capillary platform and the supporting equipment platform, and (4) the design and construction of suitable probes used to collect vapors. In particular, the portable PLOT-cryo capillary platform must be made field operable and robust (i.e., without the amenities of the laboratory), the supporting equipment platform must be made lightweight, portable and robust, the service interface between the PLOT capillary must be made flexible and efficient, and a selection of standoff probes of different sizes and configurations to allow sampling in soil, under concrete slabs, in tanks, freight containers, motor vehicles, etc., must be available and reliable.

2. Materials and methods

As introduced above, the portable PLOT-cryo apparatus consists of four aspects: a field capable PLOT-capillary platform, the supporting equipment platform, the service interface between the PLOT-capillary and the supporting equipment, and the necessary peripherals. These will be treated separately in the following section.

2.1. Field capable PLOT-capillary

Two separate devices for effectively and conveniently holding the PLOT capillary during use in the field have been developed: the hand piece and the standoff module. Both approaches are dependent upon the encapsulation of the capillary in an epoxy wafer; this device and the process used in its fabrication shall be discussed first.

2.1.1. Single PLOT-capillary wafers

Unlike the use of PLOT-cryo in the laboratory, field use demands a much higher level of robustness and convenience. To achieve this, the PLOT capillary was embedded in a polymer wafer composed of a thermosetting high strength polymer (made by combining polyepoxides with a polyfunctional hardener). Embedding the PLOT capillary in this way serves several purposes. First, it allows the capillary to be handled as a single rigid unit instead of as a flexible fiber. Second, it provides an additional protective layer to supplement the polyimide coating that is already applied to the capillary. Third, it facilitates temperature control (both heating and cooling) in that the entirety of the PLOT capillary occupies a small, fixed geometry around which the temperature controlled air flow may be optimized. Embedding the PLOT capillary is done by first forming a coil of a 1 m length of the PLOT capillary with the desired adsorbent phase, and fastening the coil diameter with a 1 cm length of heat shrink tubing. The diameter of this coil is typically 5–6 cm. This method of coil formation is the same as that used for the preparation of PLOT capillaries for the laboratory. To fabricate the wafer, the coiled capillary is then snapped into a three-sided PTFE mold that can be completely dismantled [35]. A photograph of this mold with a PLOT capillary in place is provided in Supporting information, Fig. S1. To form the embedded capillary wafer, approximately 20 mL of a mixture of equal parts polyepoxides and polyfunctional hardener is mixed in a disposable mixing boat for approximately 1 min. This viscous (but still fluid) mixture is then poured into the mold completely covering the PLOT capillary, whereupon the mixture polymerizes in approximately 5 min. Care must be taken at this point not to attempt fine adjustments to the position of the PLOT capillary because the polymerizing mixture will get quite warm (to the touch). In Supporting information, Fig. S2 provides an image of a wafer in which a PLOT capillary has been embedded.

If the wafer is to be used with the hand piece, it is not necessary to incorporate any connection fittings to the capillary, since one end of the capillary itself serves as a vapor probe. For connection to the standoff module, stainless steel tube-stub union fittings are embedded with the capillary. The fittings used were commercial 304 stainless steel tube stubs (a male compression fitting for 0.0158 cm, 0.0625 in. nominal, at one end, and a straight length of tube, 0.3175 cm, 0.125 in. nominal, at the other end) that were modified to allow the polymer to seal the capillary and the tube stub of the fitting. The modification consists of grinding part of the length of the tube stub into a half-cylinder, as shown in Supporting information, Fig. S3. When the fittings are slipped over the ends of the PLOT capillary held in the mold, the halved out stub serves as a tray that contains the epoxy, and seals the capillary, fitting and wafer into a single unit. During the fabrication, excess length of PLOT capillary is allowed to extend out of the compression fittings; the excess is trimmed after the polymerization of the module is complete. This is done by cleaving the capillary ends at the base of the conical section of the compression fitting by use of a modified dental explorer, shown in Supporting information, Fig. S4. This instrument was hollow ground to form a cleaving surface by use of an abrasive cutoff wheel to incorporate a sharp burr at the end. Cleaving the fused silica capillaries at the base of the cone essentially forms a zero dead volume connection to any union that is affixed to the capillary PLOT wafer.

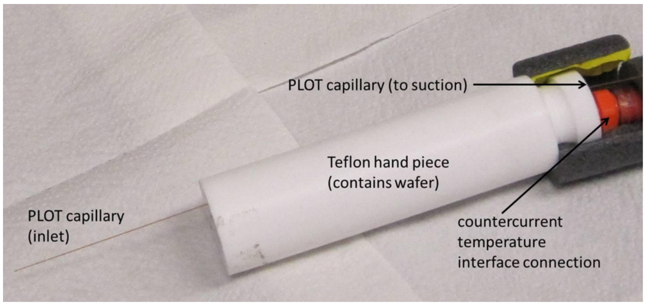

Fig. 1. A photograph of the Teflon hand piece containing the PLOT capillary embedded in an epoxy wafer.

Once the PLOT capillary is embedded into an epoxy wafer, it is ready to be installed into either the hand piece or the standoff module. The single capillary embedded in the wafer is adequate for many sampling tasks especially when a high throughput is not an issue.

2.1.2. *Multiple PLOT-capillary wafers*

The wafer construction describe above utilized a single PLOT capillary. For many vapor sampling problems, a higher throughput of vapor into the collection device (than is provided by the single capillary, above) is desirable. Moreover, a higher capacity for analyte is often needed. This is provided by simple modifications to the above wafer construction procedure by allowing at least six PLOT capillaries to be bundled into a wafer. To accommodate the additional capillaries, the channels of the tube stub fittings (with the half cylinder already ground into the stub end) are bored to a diameter of 1.5875 mm (0.0625 in., nominal). As with the single capillary units, the multiple capillaries are snapped into the PTFE mold with the fittings in place. The epoxy wafer is made with the same molding process as discussed above, and the excess length of PLOT-capillary that extends out of the compression fittings is cleaved with the hollow ground dental explorer. While in principle the number of individual PLOT capillaries is limited only by the desired size of the resulting wafer, a six capillary wafer was found to perform very well, was compact and easy to construct.

A completed six capillary wafer is shown in Supporting information, Fig. S5. Note that the hardened wafer can be machined by drilling, milling or turning to achieve a desired geometry. Moreover, it is tough (with an average measured Vickers hardness number of 46 ± 3), and can withstand dropping from a lab bench to a concrete floor without breaking or chipping.

For both the single and multiple PLOT-capillary wafers discussed above, thermosetting high strength epoxy has been the material of choice primarily because of ease of use and favorable mechanical and thermal properties. It should be noted that other materials can be used, such as single part (moisture cure) and two part silicone polymers. Experiments with these monoliths are currently in progress.

2.1.3. *Hand piece*

A prototype hand piece is shown in Fig. 1, where the PLOT capillary inlet and outlet, the suction connection and the countercurrent service interface connection to the temperature controlled air (for both cooling and heating, which will be described in detail later) can be seen. Although not visible in the photograph, the air enters the hand piece through a delivery catheter that is perforated over its length so that the temperature controlled air is released over the entire length of the wafer. The hand piece itself was made from a cylinder of Teflon (2.5 cm diameter) that was bored out to accommodate the entire epoxy wafer. The space inside the hand piece allows free circulation of the temperature control air. Since the unit is made from Teflon, which provides insulation, the hand piece can be held comfortably even when the wafer is being heated or cooled. A length of the PLOT capillary extends from the front of the hand piece, for sampling of vapors, and a length extends from the rear of the hand piece, for the application of suction. This feature of the hand piece allows the PLOT capillary to probe vapors directly, with no additional components or hardware. At the rear of the hand piece is a barbed fitting that connects to the service interface; this is the means to join the hand piece to the supporting equipment platform, which will be discussed later. Also, at the rear of the hand piece is the length of capillary that will connect to the suction port (mentioned above). This port provides the negative pressure needed to draw vapor into the PLOT capillary in order to collect vapor analytes. The suction port connection, shown in Supporting information Fig. S6, consists of a polyethylene septum vial that has been bored out to receive a vacuum line (from the vacuum generator in the supporting equipment platform, to be discussed below). This vial provides a leak tight connection to the fused silica PLOT capillary, but also allows an activated carbon bed to be placed before the vacuum line. This minimizes the potential of breakthrough vapors from reaching the vacuum generator (located in the supporting equipment platform).

While all work done thus far with the hand piece utilized Teflon as the housing material, it should be noted that any insulating material that is easily machined can be used as well.

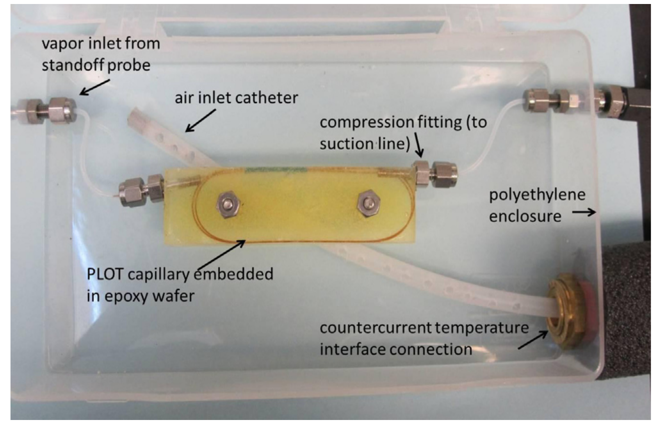

Fig. 2. A photograph of the standoff probe module containing a (single) PLOT capillary embedded in an epoxy wafer, mounted inside of a high density polyethylene enclosure.

2.1.4. *Standoff module*

The connection to the standoff probes (discussed below) is somewhat more complicated than the hand piece discussed above because these probes must penetrate more deeply into soil, cargo containers, luggage, etc. They should be of sufficient strength and rigidity, and of variable length to provide optimum adaptability. Because of these considerations, the connection to the standoff probes requires the rigidity provided by compression fittings, as discussed above. A photograph of the standoff probe module are provided in Fig. 2, showing the PLOT capillary wafer and support, the air delivery catheter, the countercurrent temperature connection, and the inlet/outlet lines. All of these components are mounted inside of a high density polyethylene enclosure. Note that the catheter shown in Fig. 2 is the same type as that used for the hand piece. In this photograph, the perforations along the length of the catheter are clearly visible. This catheter is placed below the PLOT capillary wafer, with access provided by ceramic supports. Insulation is provided for the box by a wool "sweater" that has been knitted as a sleeve, which can be slipped over the box.

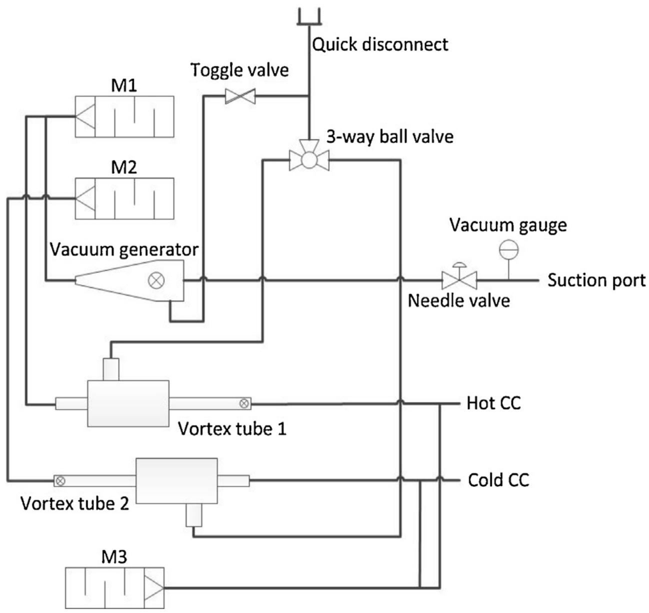

Fig. 3. A flow diagram of the support platform that operates the field-portable PLOT-cryo unit. In the diagram, M1, M2 and M3 are mufflers, and the hot CC and cold CC refer to the countercurrent connections.

2.2. The supporting equipment platform

The supporting equipment platform consists of the means for generation of the cold air stream (for cryoadsorption), the hot air stream (for thermal desorption or to assist with solvation of the collected analytes) and suction (for mass transfer). A flow diagram for the supporting equipment platform is shown in Fig. 3. A photograph of the unit is provided in Supporting information, Fig. S7. The platform consists of a quick disconnect fitting for attachment to a source of compressed air, a vortex tube to generate cold air, a vortex tube to generate hot air, a pneumatic vacuum generator to produce suction (which, along with a needle valve and vacuum gauge provides stable suction control and monitoring), mufflers, and associated insulated transfer lines. More conventional temperature control methods are not suitable because both heating and cooling are required, and because the irregular shape of the PLOT module does not lend itself to piezoelectric cooling or a circulating heat transfer fluid. Moreover, as mentioned in the introduction, the use of compressed air eliminates the potential of spark sources and allows the operation in explosive atmospheres (including class 1, division 1, groups A and B locations as specified by the National Electrical Code) [10].

Connection to the compressed air source should be made with a flexible polyurethane hose (rated for 2000 kPa) and not a semi-rigid, self-coiling hose, which can be brittle and prone to rupture. While remote sources of compressed air are universally available on fire apparatus and on many law enforcement vehicles, the quality of the compressed air requires consideration. The compressed air source should ideally be clean and dry, and be available at a service pressure of 690–830 kPa (100–120 psig). Operation below this pressure range is possible, however the ultimate high and low temperatures obtainable will have to be de-rated. Operation above this pressure range is also possible, provided the pressure ratings of the tubing and connections are not exceeded.

It is important that the compressed air be free of liquid water or water mist, and also free of oil, rust and other particles. Thus, a particulate filter and a coalescence filter upstream from the connection (labeled the quick disconnect in Fig. 3) is recommended. Such a filter is often present on the compressed air cock on fire apparatus; that, in combination with the typical automatic blow-down (that is typically done at intervals of 1.5 min at the compressed air receiver tank) will minimize the presence of liquid water and oil. Similarly, one should not use a compressed air source that is connected to an automatic air oiler. If the air is oiled, a coalescence filter must be located downstream from the oiler. Water vapor is ubiquitous in compressed air systems, even in laboratory installations with chilled water after-coolers and refrigerated driers. Operation of the vortex tubes for extended periods of time, especially in high ambient humidity, can result in the formation of ice dams in the cold air outlets. If this happens with the portable PLOT-cryo unit, the dam can often be cleared by briefly blocking the flow from the countercurrent fitting with the palm of a hand. If this interruption in flow does not clear the dam, then the air must be turned off for 5 min to allow the ice dam time to melt. Ice formation that occurs on the exterior of the cold countercurrent fitting is not a problem and does not require clearing for proper operation.

The vortex tubes and the pneumatic vacuum generator are all commercial devices that have been optimized for their application to the portable PLOT-cryo apparatus. The cold air vortex tube is tuned to provide the lowest attainable temperature by use of a vortex generator with a small aperture, and by adjusting the exit valve (shown on the vortex tubes in Fig. 3) to high flow. The hot air vortex tube is tuned to provide the highest possible temperature by use of a vortex generator with a large aperture, and adjusting the exit valve to a low flow. Note that for both the cold air vortex tube and the hot air vortex tube, the exit valves are located on the hot air end of the tube. On the cold air vortex tube, the hot air is discarded to exhaust, while on the hot air vortex tube, the cold air is discarded to exhaust. Once set to optimum, there is no need for any further changes to the settings on either vortex tube. Indeed, the reason that two vortex tubes are used in the portable apparatus, while only one is used in the typical laboratory installation, is to avoid the need for any operator adjustments when in the field. The reason that two separate countercurrent fittings are used for the hot and cold streams is to prevent pneumatic crosstalk through muffler M3. The vacuum generator is tuned to provide maximum suction, and control is provided to the operator by use of the needle valve and gauge.

The custom made countercurrent fitting that connects the supporting equipment platform to the service interface (described in the next section) is shown schematically in Fig. 4. It was made from a brass "T" compression bulkhead fitting (0.95 cm, 0.375 in. nominal) that was modified by brazing a machined chamfered insert (0.64 cm,¼ in. nominal, also made from brass) in the bottom of the straight portion, below the diverging branch. The inside surface of this insert was polished to gloss to facilitate insertion of the air delivery tube, and to maintain a good seal.

The connections among the components shown in Fig. 3 are as short as possible and are insulated with foam tubing to minimize heating and cooling losses. The components of the control platform are surrounded by sound control sheets (made from lead layered polymeric foam) to control noise. These sound control sheets were previously designed specifically for vortex tube applications [36]. The entirety of the supporting equipment platform is contained inside of an aluminum briefcase of the type used to carry field service tool sets. This provides a sturdy, light weight container that is easily carried from location to location.

2.3. Service interface

For operation, a service interface between the supporting equipment platform and the vapor collection devices (the hand piece or the standoff modules) is required. The purpose of the service inter-

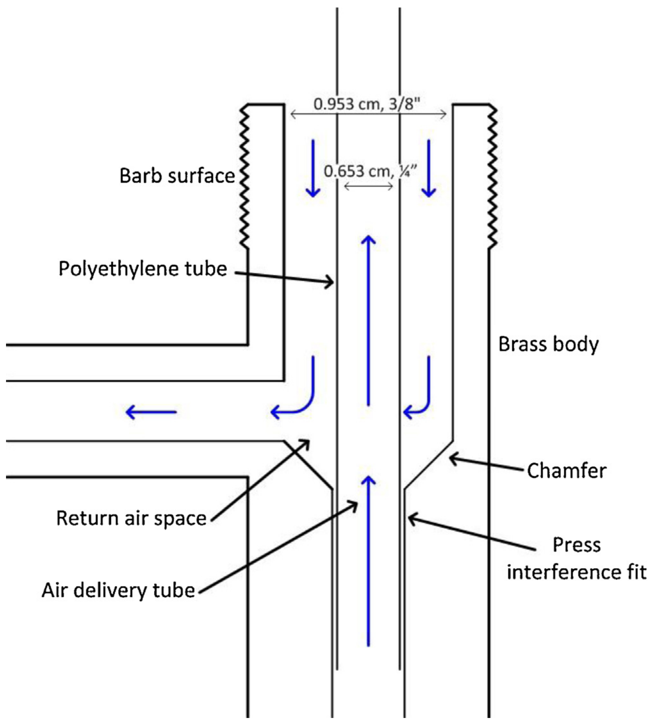

Fig. 4. A schematic diagram of the connection to the (countercurrent) service interface used to supply hot and cold air to either the hand piece or the standoff module.

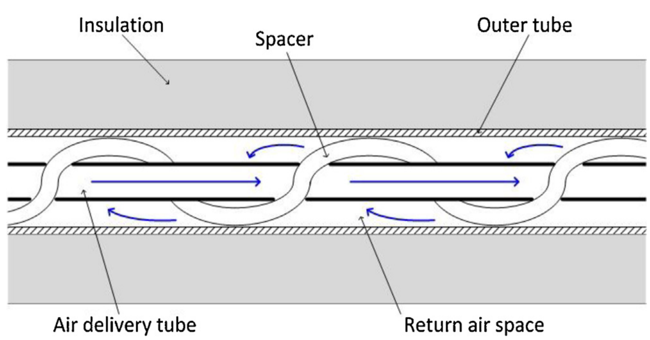

Fig. 5. A schematic diagram of the service interface that connects the hand piece or standoff module to the countercurrent fitting.

face is to deliver temperature control of the PLOT capillary wafer (in the hand piece or standoff module). The interface line itself consists of the central tube, a helical spacer, an outer sheath, and a layer of polymeric foam pipe insulation, as shown schematically in Fig. 5, and photographically in Supporting information, Fig. S8. The central tube (made from semi-flexible polyethylene) is the air delivery line, which carries the cold air (from the cold air vortex tube) or hot air (from the hot air vortex tube) to the PLOT capillary. The typical dimension of this line is 0.64 cm (¼ in. nominal) outside diameter. The helical spacer is a section of flexible tubing with a nominal outside diameter of 0.95 cm (0.375 in. nominal); it is wound about the central tube to provide the countercurrent return air with a flow path that is free of obstruction and choking. It also minimizes contact of the delivery line with the outer sheath. The outer sheath is a section of flexible tubing with an outside diameter of 1.91 cm (0.75 in. nominal) and an inside diameter of 1.27 cm (0.5 in. nominal). It contains the central tube and the helical spacer, providing containment to the countercurrent streams. The layer of pipe insulation shields the countercurrent flows from the surroundings.

During operation, the service interface is attached to either the cold or hot countercurrent connection (the connector is shown schematically in Fig. 4), depending on whether cooling or heating is desired. This fitting is specially designed to provide a flow of temperature controlled air that is jacketed and insulated by the spent or return air stream. This is referred to as recuperative thermostatting. For example, when using the cold air vortex tube (see Fig. 3) for chilling the PLOT capillary, cold air travels within the central tube (the delivery line) to cool the PLOT-cryo wafer (in the hand piece or the standoff module). The exhaust air, instead of being discharged out of the hand piece or standoff module, is routed back around the delivery line to provide insulation (with cold air) and to minimize loss of cooling due to heat transfer from the surroundings. The air is in fact returned to the supporting equipment platform through the connection shown in Fig. 4, whereupon it is routed into muffler M3 and discharged inside the aluminum carry case. The sound of the discharging air is muffled by the lead lined sound control sheets described earlier. For the delivery of hot air to the PLOT capillary (for analyte desorption), the same service interface line is used, but it is connected to the (separate) countercurrent connector fitting that is affixed to the hot air vortex tube. Thus far, interface lines of 3 and 5 foot lengths have been used. The longer interface is capable of routinely providing a cold air stream of −10 °C, while the shorter one can routinely provide −20 °C. When the hot air stream is used, the shorter interface line can deliver air at 80 °C, while the longer one can deliver air at 70 °C. The temperature reproducibility in each case is 1 °C. The suction line that is visible in Fig. S8 connects the PLOT-cryo capillary (in either the hand piece or the standoff module) to the vacuum generator in the control platform, as shown in Fig. 3.

2.4. Standoff probes

While the hand piece can be used as a stand-alone means of collecting a vapor sample, a distinct advantage of the PLOT-cryo method is that it is amenable to use with standoff probes. Standoff probes can be used to sample the vapor space remotely and in greater safety. One can use a standoff probe to sample the vapor inside of a suitcase or shipboard cargo container, through soil or through a hole or gap in a concrete slab or wall. Two different types of standoff probes have been designed and constructed for use with the portable PLOT-cryo. In any approach to the design of a standoff probe, attention must be paid to the surface of the transfer line that is chosen to transport vapor from the sampled environment to the PLOT capillary. The surface must be inert and must interact minimally with the vapors being collected. Moreover, the standoff probe must be rigid, robust and able to withstand rough handling. For these reasons, a metal standoff probe is desirable. It is possible to chemically passivate metal surfaces, but this is unlikely to provide a sufficiently inert surface [37]. Commercial processes are available to silanize the interior of metal tubes, also with mixed and often disappointing results [38]. The standoff probes developed for use with portable PLOT-cryo are therefore lined with a fused silica tube, sealed inside of 316 stainless steel jacket. The jacket has an outside diameter of 0.32 cm (0.125 in. nominal), and an inside diameter of 0.076 cm (0.030 in. nominal), and the fused silica liner inserted into the jacket has an inside diameter of 850 μm. The fused silica surface is good for general purposes (ambient temperature, analytes of low to moderate polarity, for example), however other surface materials or treatments might be indicated in particular circumstances. If vapors are to be sampled from high temperature environments, the catalytic activity of the surface might have to be considered, since it is a Lewis acid.

Thus far, two types of probe have been developed and constructed. The first incorporates a crimp type septum cap to connect to the PLOT capillary of the hand piece shown in Fig. 1. The second

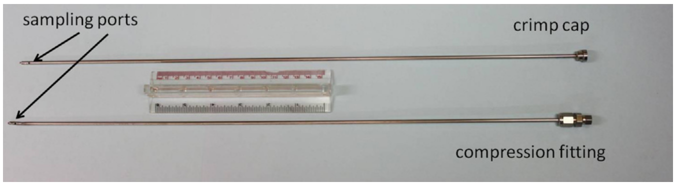

Fig. 6. A photograph of the standoff probes that are used to sample vapors. A 15 cm scale provides perspective.

probe incorporates standard compression fittings that allow connection to the standoff module shown in Fig. 2. A photograph of both types of probes is shown in Fig. 6. The overall length of the probes used thus far is 35.6 cm (14 in. nominal), a length chosen to allow the probes to be placed diagonally inside the aluminum carry case (with service interface and all peripherals) for easy transport. The probe equipped with the crimp cap is limited to this length, however the probe equipped with the compression fittings can be used to assemble multiple lengths and therefore provide an overall length on the order of 1–2 m.

2.5. Operation of the portable PLOT-cryo apparatus

The details that have been provided above have been sufficiently detailed that only a few additional operational aspects will be noted here. The hose connecting the supporting equipment platform to the compressed air source is affixed after first ensuring that both the toggle valve (that controls suction) and the 3-way ball valve (that controls temperature) are in the "off" positions. To chill either the hand piece or the standoff module, the service interface is connected to the cold countercurrent fitting, and the ball valve is set to deliver air to that fitting. If one of the standoff probes is being used, then it should be fastened to the standoff module by tightening the compression fitting. We have found that even with stainless steel connections, firm finger tightening is adequate. Cooling the PLOT capillary will require between 5–10 min, depending upon ambient conditions. While both the hand piece and the standoff module have a thermocouple access to monitor temperature, routine temperature measurement, or a precise knowledge of the temperature, is not necessary for typical operations. When the PLOT-capillary is cold, the toggle valve to the vacuum generator is switched to the "open" position. Suction is adjusted with the needle valve to achieve a vacuum level of −10 kPa (−30 in.-Hg nominal).

The flow rate through either the single or multiple PLOT capillary wafers will be dependent on a number of factors. While a mechanical vacuum pump might provide a high vacuum and therefore a relatively high flow rate, portability dictated the use of the air operated vacuum generator. To approximate the flow rate that could be achieved (assuming air as the vapor stream being sampled), a temperature compensated, primary flow meter based on positive volume displacement capable of operating in a positive or negative pressure mode was used. For a single capillary wafer, a flow rate of 30 ± 2 mL/min is typical. For the six capillary wafer, the typical flow rate at ambient temperature was 180 ± 4 mL/min. Note that this is in the as-fabricated condition. The actual realized flow rates of these devices are dependent on the ambient air temperature and pressure, and air moisture content. In addition, the flow rate will be dependent on the condition, usage and history of the PLOT capillary(ies).

Once the PLOT wafer is cold, the inlet port (of the PLOT capillary from the hand piece or the standoff probe) is placed into the environment of the vapor to be sampled, and the toggle valve to suction is opened. Sampling periods of 3, 10 and 30 min have been used in past laboratory work with PLOT-cryo, however some experimentation might be needed to determine appropriate collection time periods under field conditions. When vapor sampling is complete, the ball valve is turned to the "off" position, the suction valve is placed in the off position, and the service interface is placed on the hot countercurrent fitting. The ball valve is then turned to the "hot" position, and once warm, the PLOT capillary is eluted with an appropriate solvent.

A union fitting to connect a Luer taper with a compression fitting allows connection of the PLOT capillary to a syringe. The solvent volume (typically 1–1.5 mL) should be backed with an approximately equal volume of air to ensure that the all solvent passes through the PLOT column and is transferred into the automatic sampler vial. When using the standoff probes, one notes that the probe becomes cold for a few centimeters nearest the module. It is therefore possible for some vapor to condense in the top of the probe, just before reaching the adsorbent in the PLOT capillary. For this reason, the standoff probe should be left in place during the solvent rinse to recover any analyte that may have accumulated. Once the solvent rinse is completed and the sample is sealed with a septum cap, the capillary is activated for the next use. With the ball valve turned to the "hot" position, the suction toggle valve is activated. The hot air that flows to the PLOT capillary facilitates residual solvent evaporation and helps to reactivate the adsorbent for the next use. This can be done in a few minutes, thus it is possible to collect numerous samples in a workday. These samples may be accumulated in automatic sampler vials and returned to the laboratory for any appropriate analysis, or measured immediately with field- portable chemical analysis instrumentation.

While the solvent elution method presented above results in sample presentations that are familiar and easy to handle, it should be noted that solvent-free operation is also possible with the portable method. The hot air furnished by the vortex tube can be used to thermally desorb more volatile solutes from the PLOT wafer, and these desorbed vapors can be inserted directly into field-portable chemical analysis instrumentation. When the hand piece is used, the length of capillary that extends from the front (for sampling) can be inserted directly into the septum port of a gas chromatograph, with a stream of carrier from the chromatograph (or from another source such as a small bicycle tire canister) used for transfer. This flowing capillary injection method had been used successfully in the laboratory for many years [39]. When the standoff module is used, a custom made fitting brazed to a syringe needle provides easy sample introduction.

3. Results and discussion

The field-portable PLOT-cryo vapor sampling apparatus, comprised of the four aspects discussed above, has been demonstrated with a number of solutes relevant to forensic and environmental analysis. These applications are discussed fully in the companion paper, Field portable low temperature porous layer open tubular cryoadsorption headspace sampling and analysis part II: applications [34].

4. Conclusion

In this paper a portable apparatus for vapor collection by PLOT-cryoadsorption was presented. The major findings upon application of the approach are:

1. A PLOT capillary encapsulated in an epoxy wafer was found to provide the robustness and convenience that would be required for portable, in-the-field use.

2. The wafer could be used in a hand piece (for manual, hand-directed sampling) or a module that attaches to a standoff probe for remote sampling.

3. By use of either the hand piece or the standoff module, the PLOT capillary can be cooled to boost vapor collection efficiency, and then heated to assist removal of the analyte. Solvent elution was found to be easily accomplished with a polyethylene syringe equipped with an easily modified Luer taper fitting.

4. A novel means of heating and cooling either the hand piece or the standoff module was provided by the recuperative thermostatting of the service interface, affixed to the custom made countercurrent fittings.

5. Analysis of the analyte recovered from the vapor was found to be readily accomplished by gas chromatography with mass spectrometry; however any applicable analytical technique can be applied to the solution. While all of the work discussed here was done with solvent eluted samples that were ultimately analyzed in the laboratory, the method can be used with thermal desorption directly into a field-portable chemical analysis instrument, as applicable.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chroma.2015.12.013.

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