

A combinatorial approach to screening carbon based materials for respiratory protection

J.V. Romero^a, J.W.H. Smith^a, C.L. White^a, S. Trussler^a, L.M. Croll^b, J.R. Dahn^{a,*}

^a Department of Physics and Atmospheric Science, Dalhousie University, 6300 Coburg Road, Halifax, Nova Scotia, Canada B3H 3J5

^b 3M Canada Company, Brockville, Ontario, Canada K6V 5V8

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ABSTRACT

A combinatorial materials science approach for the discovery of an impregnated activated carbon that can adsorb a wide variety of toxic gases (i.e. a multi-gas carbon) has been developed. This approach presently allows for the parallel preparation and investigation of 64–100 IAC samples at once increasing the rate of discovery of viable multi-gas carbons. Multi-gas carbons were prepared using a solutions handling robot and screened gravimetrically for their effectiveness as gas adsorbents. The method was validated using known gas adsorbent materials such as ZnCl₂, K₂CO₃ and CuO-impregnated carbons. The calculated adsorption capacities and stoichiometric ratios of reactions for these known gas adsorbent materials, when evaluated using the combinatorial approach, was comparable to the values obtained using traditional methods of analysis. A library of samples prepared by combining various amounts of CuO and ZnO impregnants showed the expected decreasing trend in the calculated stoichiometric ratio of reaction with respect to increasing amount of impregnants added. The method is now ready to use to explore new systems of impregnated activated carbons.

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1. Introduction

Activated carbon has long been used as a gas adsorbent for respirator applications. Impregnated activated carbon (IAC) is normally the material of choice for the adsorption of toxic gases [1,2].

Activated carbon adsorbs impurities such as organic vapors on surfaces in its large network of channels and pores. However, untreated activated carbon poorly adsorbs low molecular weight, highly polar gases such as HCN, SO₂ and NH₃. Adsorption of these gases onto activated carbon can be enhanced by chemical treatments that either lead to an increase in surface oxide groups or by the addition of reagents that are able to react with these toxic gases. Increasing the amount of oxygen on the surface of the carbon can be achieved using oxidizing agents such as ozone, CO₂, HNO₃, NaClO and H₂O₂. Such surface treatments greatly improve the adsorption capacity of the carbon for acidic and basic impurities in gas streams [2–8]. Adding impregnants that react with specific challenge gases, within the activated carbon pores allow these gases to be removed. One example is impregnation with either metal salts or metal oxides [2,9,10]. Addition of impregnants such as ZnCl₂ has been shown to improve the NH₃ adsorption capacity of activated carbon while addition of K₂CO₃ was reported to improve SO₂

adsorption [1,11]. Metal oxides of the first transition series were reported to be effective in the removal of SO₂ from waste gases [12,13]. Recently, CuO IAC's have been found to effectively adsorb SO₂, NH₃ and HCN gases [14,15]. The addition of several different impregnants allows a single IAC to adsorb many different toxins well [16–18].

Our goal is to find an optimum set of impregnants to apply to an activated carbon so that a specific set of toxins can be effectively adsorbed. However, finding the right combination of impregnants to prepare optimum IAC's can be time consuming. The combinatorial strategy, used predominantly in the pharmaceutical industry, has been adapted here for the preparation and screening of many different IACs simultaneously. In this paper, the method is described and examples are given for both trial and novel systems.

1.1. Combinatorial materials preparation

The combinatorial approach was introduced by Joseph Hanak in the 1970s for the preparation and screening of numerous materials simultaneously [19–21]. Since then, researchers have adopted similar strategies to explore and prepare advanced materials. Our group uses sputter deposition to prepare composition-spread thin films to be screened in battery, fuel cell and biomaterials applications [22–25]. Other researchers have used the combinatorial approach to generate libraries of materials for catalysis, high temperature superconductivity, ferroelectricity and other applications [26–30].

* Corresponding author. Tel.: +1 902 494 2628.

E-mail address: jeff.dahn@dal.ca (J.R. Dahn).

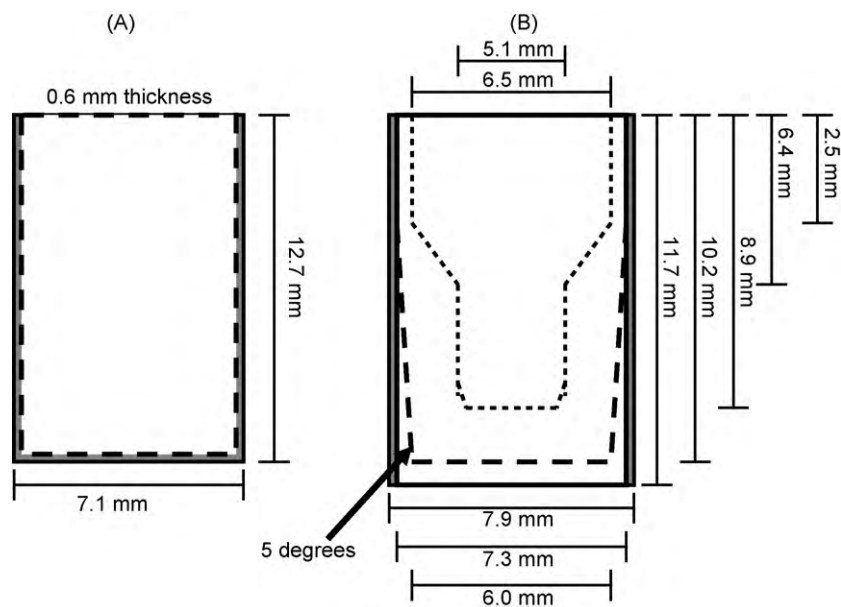


Fig. 1. A complete schematic diagram of the vial (A) and the cap (B).

For the first time, a method for preparing and screening IAC's for respirator applications by combinatorial methods is presented here. Impregnated activated carbons are prepared using a solutions handling robot. Arrays of 64 or 100 samples are prepared by dispensing varying amounts of 2 (or more) solution components on 10 mg samples of activated carbon held in microvials. A series of heating steps are employed to decompose the impregnants to the desired active phases. The effectiveness of the samples for adsorbing various toxins is screened gravimetrically by weighing the microvials containing the IAC before and after exposure to the toxic challenge gas. The stoichiometric ratio of reaction (SRR) is calculated from the recorded sample mass increase after exposure. The SRR quantifies the material's ability to filter toxic gases.

The method has also proven to be cost-effective in terms of man hours spent per sample as well as in the amount of starting materials used. In the traditional methods, sample preparation and testing takes about 8 h per sample while it only takes about a half an hour per sample for the combinatorial method. The combi method also requires only a fraction of the total amount of starting material that is typically used for bulk traditional preparation. This novel method of screening has the advantages of parallel preparation and investigation of a large number of samples at one time, which will increase the rate of discovery of viable multi-gas respirator materials.

2. Experimental

A conventional solutions handling robot (combi robot) was used for this study. A Cartesian PixSys™ SQ series robot, equipped with eight synQUAD™ 250 μL dispensers for handling up to eight solutions at a time, was used. The robot has a dispense deck that can accommodate up to eight 8×8 , 8×12 or 10×10 arrays of sample holders, a wash station and a vacuum station to prevent solution crossover. The robot can dispense solution volumes ranging from 0.2 to 250 μL with high precision and accuracy. The instrument comes with the AxSys™ software that allows the robot to be programmed to dispense according to our specific needs. The ease of programming also allows versatile adjustments of the volumes (and stoichiometries) of solutions being dispensed.

The prepared samples were analyzed gravimetrically using a Sartorius SE-2 microbalance that measures a maximum mass of 2.1 g and has a resolution of 0.1 μg . The balance is connected to a

computerized workstation to automatically record the data onto an Excel spreadsheet.

Gravimetric measurements of activated carbon samples are non-trivial due to their tendency to adsorb moisture rapidly from the air. For this reason, custom vials to hold the IAC samples were designed. These vials needed to satisfy several requirements:

1. capable of withstanding temperatures up to 300 °C without mass change,
2. ability to be capped and uncapped conveniently with tight-fitting caps to eliminate moisture uptake during weighing,
3. corrosion resistant in the case acidic impregnants are employed, and
4. total mass of vial and cap to be less than 2.1 mg for compatibility with the microbalance.

Deep drawn stainless steel (grade 304) cylindrical vials with dimensions of 12.7 mm height and 7.1 mm diameter having a wall thickness of 0.6 mm were obtained from Hudson Technologies. The caps were machined in-house from aluminum rod and thin walled Al tubing. A solid piece of aluminum rod, tapered at one end (7.3 mm diameter) was press fit into a pre-cut piece (7.3 mm I.D.) of aluminum tubing as shown in Fig. 1. Once fitted, the untapered side of the rod was drilled to reduce the mass of the cap. Fig. 1 shows a complete side-view schematic of the vial and cap. The microvial and cap together weighed an average of 1.3 g and had an approximate capacity of 0.3 mL.

To determine if the caps were air-tight, 10.0 mg of pre-dried HNO_3 -treated GC (see Section 2.2.1) were weighed into separate vials. One vial was capped and the other was left open to the environment. Mass measurements were made over a period of 2 h. Data points were taken every 3 min for the first hour and then every 10 min for the next hour. The rate of moisture uptake by the samples was determined from the slope of the curve for all the data points.

It should be noted that both polypropylene (restricted temperature-range) and Teflon (mass changes with moisture content) vials and caps were tried and discarded before the stainless steel/aluminum solution was perfected.

2.1. Sample preparation

A commercially available coconut-shell based granular activated carbon (called “virgin GC” in this paper) was obtained from Kuraray Chemical Co. The carbon contains 0.4% (w/w) ash, is slightly basic with a pH of 8 (measured after immersion in nanopure water) and has a mesh size of 12×35 , which corresponds to particles between 0.50 and 1.70 mm in diameter [1,31]. Bulk pre-treatment of all activated carbon samples was performed using a procedure previously reported in literature and often referred to as the incipient wetness or imbibing method [11,28,31]. The same method was also employed to impregnate the pre-treated activated carbon samples with impregnant solutions using the combi robot.

2.2. Bulk preparation of $\text{Cu}(\text{NO}_3)_2$ and $\text{H}_3\text{PO}_4(\text{MoO}_3)_{12}$ -impregnated activated carbons

2.2.1. Bulk preparation of $\text{Cu}(\text{NO}_3)_2$ and $\text{H}_3\text{PO}_4(\text{MoO}_3)_{12}$ -impregnated activated carbons by the sequential addition method

Bulk impregnated activated carbon materials were prepared according to a modified procedure described in literature [14,32]. Previously dried virgin GC (10.0 g) was pre-treated with 8.0 mL of 4.0 M HNO_3 (Fisher) solution. The acid-treated carbon was dried in air at 140 °C for 30 min and then at 180 °C for 2 h. An average mass increase of 4.0% for the activated carbon samples was recorded after HNO_3 treatment. The resulting product is called HNO_3 -treated GC henceforth.

Two sequentially bulk impregnated samples were prepared. 10.4 g of HNO_3 -treated GC, was sequentially impregnated first with 5.10 mL of 3.50 M $\text{Cu}(\text{NO}_3)_2 \cdot 2.5 \text{H}_2\text{O}$ (Aldrich) followed by the addition of 2.70 mL of 0.100 M $\text{H}_3\text{PO}_4(\text{MoO}_3)_{12} \cdot 25 \text{H}_2\text{O}$ (PMA) (Alfa Aesar) and is henceforth referred to as Sample # 1. Another 10.4 g sample of HNO_3 -treated GC was impregnated with 2.70 mL of 0.100 M PMA first followed by the addition of 5.10 mL of 3.50 M $\text{Cu}(\text{NO}_3)_2 \cdot 2.5 \text{H}_2\text{O}$ and is henceforth referred to as Sample # 2. The impregnated samples were shaken for about 5 min to ensure complete imbibing of the impregnating solutions. After shaking the samples, the lids were removed and a visual determination of a completely imbibed sample such as described in Ref. [14] was made. In addition, the activated carbon samples appeared to have absorbed all the impregnating solution since no liquid remained at the bottom of the vial upon visual inspection. The samples were placed inside alumina boats and then dried inside a Lindburg tube furnace under argon (Praxair) for 30 min at 110 °C. The temperature was then increased to 200 °C for 2 h. This heating step completely converts the $\text{Cu}(\text{NO}_3)_2 \cdot 2.5 \text{H}_2\text{O}$ to CuO and dehydrates the $\text{H}_3\text{PO}_4(\text{MoO}_3)_{12} \cdot 25 \text{H}_2\text{O}$. After 2 h, the power to the furnace was turned off. The samples inside the furnace were allowed to cool to room temperature under a flow of argon for about 1 h before they were removed from the tube furnace. The mass of the dried samples was measured using a Sartorius BP 110 analytical balance. Total loadings of 21% and 19.4% were calculated for Sample # 1 and Sample # 2 respectively.

2.2.2. Bulk preparation of $\text{Cu}(\text{NO}_3)_2$ and $\text{H}_3\text{PO}_4(\text{MoO}_3)_{12}$ -impregnated activated carbons

A bulk impregnated activated carbon material was prepared according to the method described in literature [14,33]. Previously dried virgin GC (10.0 g) was imbibed with 8.0 mL of an aqueous solution containing $\text{Cu}(\text{NO}_3)_2 \cdot 2.5 \text{H}_2\text{O}$, $\text{H}_3\text{PO}_4(\text{MoO}_3)_{12} \cdot 25 \text{H}_2\text{O}$ and HNO_3 and is henceforth referred to as Sample # 3. The solution was prepared by dissolving 27.9 g (0.120 mol) $\text{Cu}(\text{NO}_3)_2 \cdot 2.5 \text{H}_2\text{O}$, 4.17 g (1.70×10^{-3} mol) PMA, 12.0 mL (2.90×10^{-2} mol) of concentrated (70%) HNO_3 in 50.0 mL of distilled water. The impregnated sample was shaken for about 5 min to ensure complete imbibing of the

impregnating solutions. The sample was placed inside an alumina boat and then dried inside a Lindburg tube furnace under argon for 30 min at 110 °C. The temperature was then increased to 200 °C for 2 h similar to the drying method described in Section 2.2.1. The mass of the dried sample was measured using an analytical balance. A 16.7% loading was calculated for Sample # 3.

2.3. Preparation of impregnated activated carbons by the combinatorial method

A general method for the preparation of impregnated activated carbons by the combinatorial method is described in Fig. 2 and is a modified procedure from the literature [14]. About 10 ± 1 mg of HNO_3 -treated GC was placed in pre-weighed microvials (and caps). The vials were previously cleaned and dried (120 °C, 18 h in air) before use. The HNO_3 -treated GC's were then dried in air for 2 h at 120 °C. After 2 h, the vials were capped and cooled inside a dessicator containing calcium sulfate (drierite™) dessicant (Alfa Aesar). The mass of the dried unimpregnated carbon samples were measured using the Sartorius SE-2 microbalance. Impregnating solutions were then dispensed onto the carbon samples using a solutions handling robot. The samples were capped and then shaken for 5 min to ensure complete imbibing of the impregnating solutions.

The vials containing the IAC samples were uncapped and then dried inside a Lindburg tube furnace under argon for 30 min at 110 °C. The temperature was then increased to 200 °C for 2 h. After 2 h, the power to the furnace was turned off. The samples inside the furnace were allowed to cool to room temperature under a flow of argon for about 1 h before they were removed from the tube furnace. After exposure to the air, the vials were dried once more inside an oven at 120 °C in air for a period of 4 h. Then the vials were capped inside the oven while hot and allowed to cool to room temperature in a dessicator. The masses of the dried samples were measured using the microbalance.

2.3.1. Preparation of ZnCl_2 and K_2CO_3 -impregnated activated carbons by the combinatorial method

Previously reported experiments were also used to validate the method used for challenge gas exposure tests [1,11,32]. Impregnated samples (IAC's) were prepared using a modification of the procedure described in Section 2.3. 10.0 mg of pre-dried (120 °C, 2 h, air) virgin GC was measured into empty, pre-weighed and dried stainless steel microvials. Ten replicates of each set of ZnCl_2 IAC's were prepared. Impregnation of the samples was achieved by dispensing 4.0 μL of 10.0 M ZnCl_2 (Sigma) using the solutions handling robot onto the first group of samples and then dispensing 7.0 μL of 5.0 M ZnCl_2 onto another set of 10 pre-weighed samples. The caps were then placed onto the vials and the vials were shaken for about 5 min to ensure complete imbibing of the activated carbon. The caps were removed and the samples were dried in an oven at 120 °C for 6 h in air. After drying, the caps were placed back onto the vials (inside the oven, while hot) and then the vials were cooled inside a dessicator for 1 h before measuring the dry mass of the IAC's. Control samples, where no liquids were imbibed, were also prepared in a similar manner using virgin activated carbon. Challenge gas testing of the samples in the microvials is described in Section 2.6.

K_2CO_3 -impregnated activated carbons were also used to validate SO_2 exposure tests. A modified procedure described in Section 2.3 was employed in the preparation of the K_2CO_3 IAC's. Approximately 10.0 mg of previously dried virgin GC were placed into pre-weighed stainless steel microvials. Eight replicates were prepared for each set of samples. In the first set of samples 6.0 μL of 1.0 M K_2CO_3 (Aldrich) was dispensed onto the activated carbon by the combi robot. In the second set, 2.0 μL of de-aerated distilled water was added initially onto the carbon before the subsequent

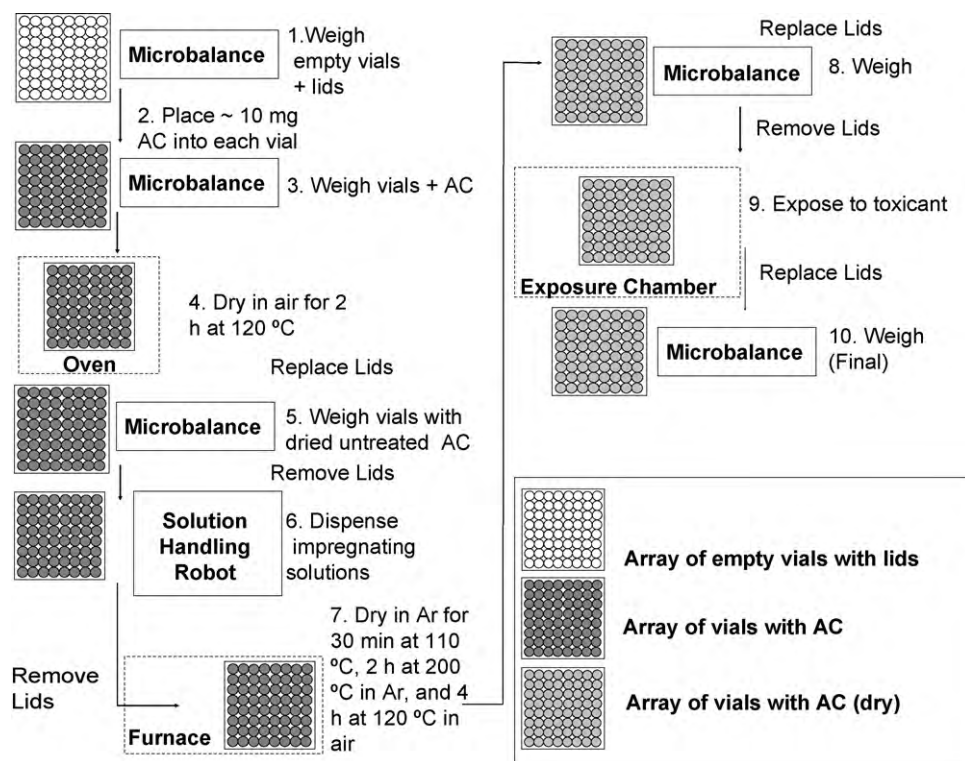


Fig. 2. A detailed process flowchart showing the sample preparation method employed in this study.

addition of 6.0 μL of 1.0 M K_2CO_3 . All caps were placed onto the vials and the samples were shaken for 5 min to ensure complete imbibing. The samples were uncapped then dried at 120 °C for 6 h in air, then the caps were placed (inside the oven while hot) and then the vials were cooled inside the dessicator for 1 h before weighing. Control samples, where no liquids were imbibed, were also prepared in a similar manner using virgin activated carbon. Challenge gas testing of the samples in the microvials is described in Section 2.6.

2.3.2. Preparation of sequentially imbibed $\text{Cu}(\text{NO}_3)_2$ and $\text{H}_3\text{PO}_4(\text{MoO}_3)_{12}$ -impregnated activated carbons by the combinatorial method

The preparation of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5 \text{H}_2\text{O}$ and $\text{H}_3\text{PO}_4(\text{MoO}_3)_{12} \cdot 25 \text{H}_2\text{O}$ (PMA) impregnated activated carbons made use of HNO_3 -treated activated GC prepared following the procedure described in Section 2.3. About 10 mg of HNO_3 -treated GC was placed in pre-weighed microvials. Two sets of sequentially impregnated samples with eight replicates were prepared. The first set was sequentially impregnated with 5.10 μL of 3.50 M $\text{Cu}(\text{NO}_3)_2 \cdot 2.5 \text{H}_2\text{O}$ first followed by the addition of 2.70 μL of 0.100 M PMA and henceforth is referred to as Sample # 4. Another set of samples was prepared by adding 2.70 μL of 0.100 M PMA first followed by the addition of 5.10 μL of 3.50 M $\text{Cu}(\text{NO}_3)_2 \cdot 2.5 \text{H}_2\text{O}$ and henceforth is referred to as Sample # 5. To ensure maximum wetness of each grain of carbon, 0.200 μL of de-aerated distilled water was added initially onto the carbon before the addition of the impregnating solutions. The impregnated samples were shaken for about 5 min to ensure complete imbibing of the impregnating solutions and were heated according to the procedure described in Section 2.3. Control samples, where no liquids were imbibed, were also prepared in a similar manner using virgin activated carbon. The samples were exposed to SO_2 challenge gas for 4 h according to the procedure described in Section 2.6.

The activities of these combi-prepared samples (Sample # 4 and Sample # 5) were evaluated against that of the bulk-prepared sam-

ples: Sample # 1, Sample # 2 and Sample # 3. Eight replicates of each sample were prepared by measuring 10.0 mg aliquots of each bulk material sample and placing them in pre-weighed stainless steel microvials. These samples were exposed to SO_2 challenge gas for 4 h according to the procedure described in Section 2.6 simultaneously with Sample # 4 and Sample # 5. A summary of the impregnation method and the order of impregnant addition in each sample is given in Table 1.

2.3.3. Preparation of $\text{Cu}(\text{NO}_3)_2$ and $\text{H}_3\text{PO}_4(\text{MoO}_3)_{12}$ -impregnated activated carbons by the combinatorial method for a 1-dimensional experiment

The preparation of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5 \text{H}_2\text{O}$ and $\text{H}_3\text{PO}_4(\text{MoO}_3)_{12} \cdot 25 \text{H}_2\text{O}$ (PMA) impregnated activated carbons made use of HNO_3 -treated activated GC and employed a modification of the procedure described in Section 2.3. About 10 mg of HNO_3 -treated GC was placed in pre-weighed microvials. Increasing volumes (1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0 μL respectively) of a 3.5 M solution of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5 \text{H}_2\text{O}$ were first dispensed using the combi robot onto the HNO_3 -treated GC's. The $\text{Cu}(\text{NO}_3)_2 \cdot 2.5 \text{H}_2\text{O}$ -containing samples were then impregnated with decreasing volumes (7.0, 6.0, 5.0, 4.0, 3.0, 2.0, 1.0 and 0.0 μL respectively) of a 0.1 M solution of PMA resulting in eight IAC samples with three replicates of each. After impregnating the HNO_3 pre-treated GC's, the vials were capped, then shaken for 5 min to ensure complete imbibing of the impregnating solutions and then uncapped and heated according to the procedure described in Section 2.3.

2.4. Calibration of the dispense program for the 8×8 combi run

The program used to dispense impregnants with the combi robot was evaluated using 1.34 M zinc sulfate monohydrate ($\text{ZnSO}_4 \cdot \text{H}_2\text{O}$). Using the combi robot, $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ (Fisher) solution was dispensed into pre-weighed aluminum cups using the volumes indicated in Fig. 3. No activated carbon was included in the Al cups.

Table 1

A Summary of the method and order of impregnation of bulk and combi-prepared samples.

Sample #	Method of impregnation	Order of addition of impregnants
1	Bulk sequential imbibe	Cu(NO ₃) ₂ ·2.5 H ₂ O followed by H ₃ PO ₄ (MoO ₃) ₁₂ ·25 H ₂ O
2	Bulk sequential imbibe	H ₃ PO ₄ (MoO ₃) ₁₂ ·25 H ₂ O followed by Cu(NO ₃) ₂ ·2.5 H ₂ O
3	Bulk traditional	Pre-mixed Cu(NO ₃) ₂ ·2.5 H ₂ O and H ₃ PO ₄ (MoO ₃) ₁₂ ·25 H ₂ O solution
4	Combi sequential imbibe	Cu(NO ₃) ₂ ·2.5 H ₂ O followed by H ₃ PO ₄ (MoO ₃) ₁₂ ·25 H ₂ O
5	Combi sequential imbibe	H ₃ PO ₄ (MoO ₃) ₁₂ ·25 H ₂ O followed by Cu(NO ₃) ₂ ·2.5 H ₂ O

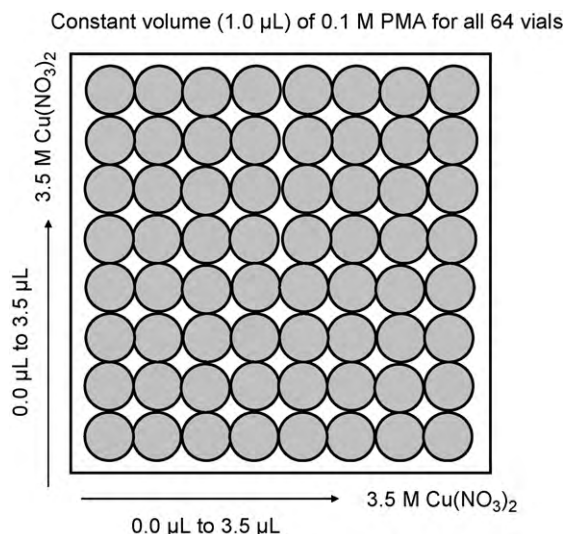
The water was then evaporated in a 120 °C oven (in air) for 2 h. The samples were then placed inside a dessicator to cool for 1 h. The masses of the salt left in the cups were measured with the microbalance.

2.5. Combinatorial preparation and of an 8 × 8 array of Zn(NO₃)₂, Cu(NO₃)₂ and H₃PO₄(MoO₃)₁₂-impregnated activated carbons

An 8 × 8 array of IAC's was prepared using the combinatorial method described and discussed previously in Section 2.3. Samples of HNO₃-treated GC's weighing approximately 10.0 mg were placed into previously cleaned and dried (120 °C for 2 h in air) stainless steel microvials. To determine the initial dry weight of the HNO₃-treated GC's, the vials containing the samples were placed inside the oven to dry at 120 °C in air for 2 h after which the vials were capped, cooled and the dry weight was measured.

Using the combi robot, increasing volumes (from 0 to 3.5 μL) of 3.5 M Zn(NO₃)₂·6 H₂O (Sigma–Aldrich) were added in increments of 0.5 μL along x-axis of the 8 × 8 array and increasing volumes (from 0 to 3.5 μL) of 3.5 M Cu(NO₃)₂·2.5 H₂O were dispensed in increments of 0.5 μL along the y-axis of the array as shown in Fig. 3. A constant volume of 1.0 μL of H₃PO₄(MoO₃)₁₂·25 H₂O (0.1 M) was added to all 64 samples. Before the addition of any of the impregnating solutions, water was added to the vials containing the pre-treated GC's using the combi robot. The volume of water added to each vial was such that the total volume of added liquids in each vial would be equal to 8.0 μL. After impregnating the HNO₃-treated GC's with the solutions, the vials were capped and then shaken for 5 min to ensure complete imbibing.

The samples were then uncapped and heated inside a Lindburg tube furnace under argon at 200 °C for 2 h using the same method described in Section 2.3. Control samples, where no liquids were imbibed, were also prepared in a similar manner using virgin activated carbon.

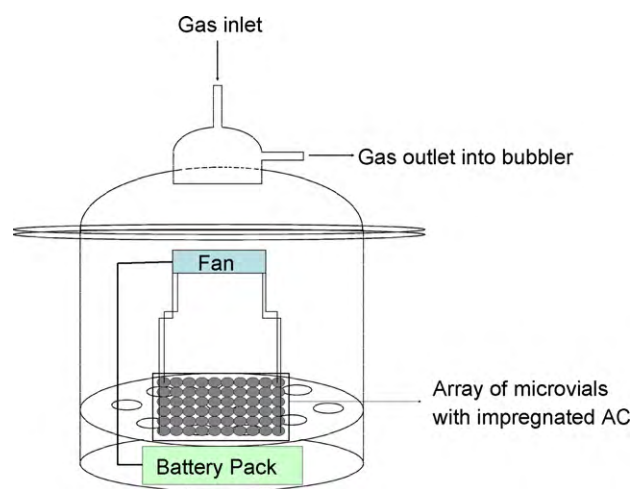
**Fig. 3.** A diagram of the combinatorial dispense method using an 8 × 8 array.

An automated uncapping/capping mechanism was used to remove and place the lids of the 64 vials in the above experiment. The mechanism uses a vacuum system to hold the vials in place while a mechanical clamp is used to lift 20 caps at the same time. The use of this mechanism minimizes the time the samples are exposed to air as they are loaded into or removed from the challenge gas exposure chamber. Once uncapped, the samples were exposed to the challenge gas for 4 h as described in Section 2.6.

2.6. Exposure of the arrays of vials to NH₃ and SO₂ challenge gases

Challenge gas exposure was performed at room temperature. Control samples were exposed simultaneously with IAC samples. Once the IAC's were completely dried and the final dry mass had been measured, the caps of the vials were removed. The vials containing the IAC's were quickly placed inside an exposure chamber built from a dessicator. The chamber was connected to a gas stream source that flowed 1000 ppm of either NH₃ or SO₂ challenge gases at a flow rate of 200 mL/min. The 1000 ppm gas stream was prepared by diluting 40 mL/min of 5000 ppm (v/v) of either NH₃ (Praxair) or SO₂ (Praxair) in dry air with 160 mL/min of compressed air (Praxair, UHP grade) at 0% relative humidity. All gases used were certified standard grade and contained less than 10 ppm each of CO₂ and H₂O. The flow rates were monitored using rotameters and mass flow controllers. A battery (12 V) operated fan was placed inside the chamber to ensure even challenge gas distribution to all samples as indicated in the sketch in Fig. 4.

The exhaust tubing from the exposure chamber was fitted with a bubbler, and the bubbler was immersed in a scrubbing solution that consisted of approximately 0.1 g KCl (BDH) dissolved in 100 mL of distilled water. To verify that the challenge gas was flowing through the chamber, the pH of the scrubbing solution was monitored using a computerized workstation.

**Fig. 4.** A diagram of the challenge gas exposure chamber is shown. The chamber is equipped with a 12 V fan to ensure gas circulation as well as a rechargeable 12 V battery pack to power the fan.

The impregnated activated carbon samples were exposed to challenge gases for 4 h. ZnCl_2 IAC's were exposed to NH_3 gas while K_2CO_3 IAC's were exposed to SO_2 at room temperature. $\text{Cu}(\text{NO}_3)_2$ IAC's were also exposed to SO_2 gas for 4 h. The combinatorially prepared 8×8 array of $\text{Zn}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$ and $\text{H}_3\text{PO}_4(\text{MoO}_3)_{12}$ IAC's were likewise exposed to SO_2 gas for 4 h and a second set of samples were exposed to NH_3 gas. After the exposure of the impregnated samples to the challenge gases, the vials were quickly capped and then weighed. The adsorption capacities and the stoichiometric ratio of reaction were calculated from the mass difference of the samples before and after gas exposure.

2.7. Analysis of the exposed and unexposed impregnated activated carbon

Exposed samples were analyzed by gravimetric, thermogravimetric (TGA) and powder X-ray diffraction (XRD) techniques. The control samples prepared on virgin activated carbon were left unexposed and were analyzed by TGA and XRD.

Thermal and X-ray analyses of the exposed impregnated carbon samples were performed. Thermal analysis (TGA) was made with a TA Instruments SDT Q600 simultaneous TGA/DSC from room temperature to about 1000°C . Samples were placed in alumina boats and heated at a rate of $10^\circ\text{C}/\text{min}$. To prevent the burn-off of the activated carbon all analysis were performed under argon gas. The samples were collected after TGA and analyzed by X-ray diffraction.

Exposed IAC samples were analyzed before and after TGA by powder X-ray diffraction (XRD) using a Rigaku MiniFlex Diffractometer. Experiments were performed at a scan rate of $0.05^\circ/\text{step}$ with a dwell time of 30 s/step. Measurements were made over a scattering angle range of $5\text{--}65^\circ$. The X-ray source was a copper tube powered at 30 kV and 15 mA. Samples were finely ground using an agate mortar and pestle before analysis. All analyses were performed in air at room temperature.

Unexposed control samples were likewise characterized by powder XRD and TGA using the same methods described above.

2.8. Confirmation of gas adsorption using soaking studies

To verify that the samples adsorbed the challenge gas, all exposed IAC samples were soaked in approximately 0.50 mL of distilled water for 10 days. After 10 days the liquid layer was collected using a Pasteur pipette and was filtered through another pipette fitted with a cotton plug. This filtration process removed any carbon dust that may be suspended in the soaking liquid. The filtrate was collected into 1/2 dram glass vials and water was removed by evaporation (120°C , air, 4 h). The remaining solid after evaporation was scraped off of the vial and analyzed by powder XRD.

3. Results and discussion

3.1. Calibration of the dispense program using $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$

For the combinatorial synthesis of IAC's it is essential to ensure that the robot delivers the correct volumes of solutions to each sample vial. To verify this, a $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ solution was used to calibrate the dispense program. The mass of the $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ salt after evaporating the solvent should give a clear picture of the precision of the combi robot dispense.

A program was written so that the amount $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ solution dispensed increased linearly along both the x - and y -directions by increments of $0.5 \mu\text{L}$. Fig. 5 shows a contour map of the obtained mass of the dried salt versus the added amount of solution. The amount of salt increases as expected and there are only small fluctuations in the contour lines. This suggests that the robot is dispensing solution precisely. This also suggests that variations in

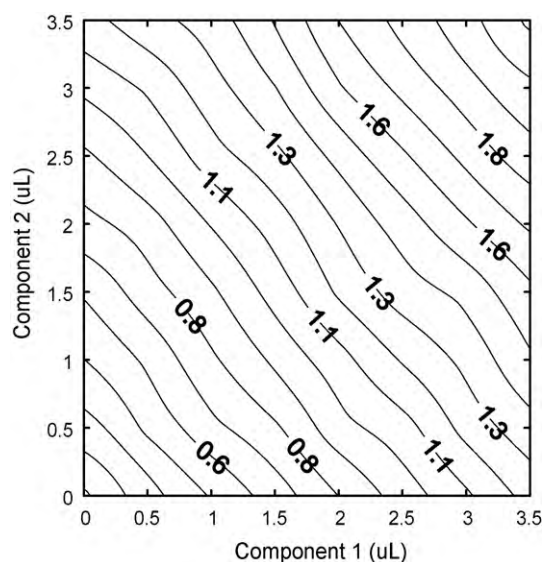


Fig. 5. A contour map showing the mass (in mg) of dried $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ salt versus the volume of solutions added in the x - and y -directions. In such a graph the contour lines should have a slope of -1 as seen from the plot.

gas adsorption that may be observed in the future experiments are material-related and not from errors made during the dispense of the impregnant solutions.

3.2. Moisture uptake evaluation

Our lid design takes into consideration the need for an airtight cap that can be removed and replaced easily with the use of our automated capping/uncapping mechanism. It is important to ensure that the cap is tight enough so that moisture uptake is minimal during the time that the samples are being weighed. We monitored the mass change of two 10.0 mg samples of HNO_3 -treated GC's placed into separate vials (one capped and the other uncapped) for a period of 2 h as described in the earlier part of Section 2. We found that the rate of moisture uptake (taken from the slope of the curve of all the data points) of the sample contained in the capped vial was slower by as much as 20 times (data not shown) compared to the uncapped sample. This indicated that moisture uptake of the properly contained sample is minimal and will not cause any significant mass changes during the screening of the impregnated samples. Therefore, we can directly relate the mass increase observed after exposure to the challenge gas to the adsorption capacity of the material.

3.3. Method validation using ZnCl_2 and K_2CO_3 IAC's

The combinatorial method for screening carbon respirator materials was tested using ZnCl_2 -impregnated activated carbon. This material is well known for NH_3 adsorption and has been reported previously in literature [1,34]. The method of impregnating a small sample of virgin GC using a solutions handling robot described in Section 2.3 and subsequent exposure (Section 2.6), was used to determine the NH_3 gas adsorption capacity of the ZnCl_2 -impregnated GC's by measuring the mass change of the impregnated samples after challenge gas exposure. Fig. 6 shows that the stoichiometric ratio of reaction (SRR), defined to be the number of moles of NH_3 captured per mole of ZnCl_2 , varies somewhat between samples. The average SRR for the ZnCl_2 -impregnated GC's was 1.68 ± 0.09 . This value is close to the reported value of 1.6 ± 0.1 obtained from flow tests on much larger samples [32]. By comparison, Fig. 6 shows that impregnation of GC using $7 \mu\text{L}$ of 5 M ZnCl_2 resulted in a calculated SRR of 1.76 ± 0.06 .

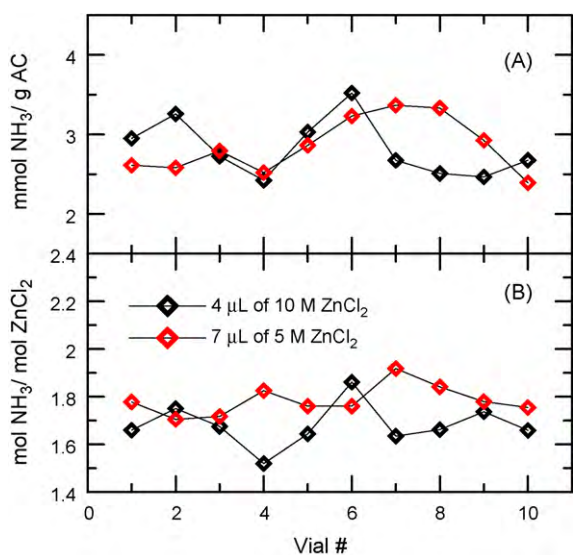
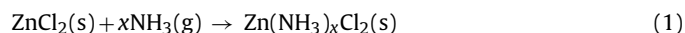


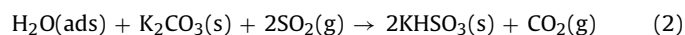
Fig. 6. The ammonia capacity of the ZnCl₂ IAC's is shown in panel A. A plot of the stoichiometric ratio of reaction (SRR) between NH₃ and ZnCl₂ with respect to sample replicates is shown in B. The calculated SRR for these experiments were 1.68 ± 0.09 or 1.76 ± 0.09 when a 4 μL of 10.0 M or 7 μL of 5.0 M solution were used respectively.

The control samples exposed to NH₃ at the same time as the ZnCl₂ IAC's did not show significant mass increases as compared with the ZnCl₂ IAC samples. This is consistent with previous observations that virgin GC has a very low NH₃ gas adsorption capacity [14,32]. Therefore the mass increase of our ZnCl₂ IAC samples can be attributed to NH₃ gas adsorption.

Stoichiometric ratios of reaction of up to 4 mol of NH₃ per ZnCl₂ have been previously reported, depending on the NH₃ partial pressure [35]. The SRR value obtained here is consistent with having x mol of NH₃ (where $x \approx 1.7$) forming a complex with ZnCl₂ according to Eq. (1) [32]:



In order to test for SO₂ adsorption, samples containing K₂CO₃-impregnated GC's were exposed to SO₂ challenge gas. According to Ref. [32], a chemical reaction occurs where 2 mol of SO₂ gas adsorb onto the K₂CO₃-impregnated carbon, producing KHSO₃ and evolving 1 mol of CO₂ gas according to the reaction represented by Eq. (2) [32]:



According to the data presented in Ref. [11], the evolution of CO₂ gas has been detected in the pH measurements of scrubbing solution further validating the reaction presented in Eq. (2). Therefore the increase in sample mass corresponds to an increase of 42 g/mol of adsorbed SO₂.

In Fig. 7, the plots show the SO₂ adsorption capacity and SRR's of the K₂CO₃-impregnated IAC's. Typically, unimpregnated activated carbon has an SO₂ adsorption capacity of about 0.3–0.4 mmol SO₂/g AC (not shown in Fig. 7). With the addition of the K₂CO₃, the SO₂ adsorption of the material increased by slightly more than twice as much as the capacity of the virgin GC. This clearly indicated that the impregnant effectively chemisorbed SO₂, consistent with literature reports [11,32]. The top panel of the graph in Fig. 7 shows that the calculated SRR between SO₂ and K₂CO₃ for IAC's impregnated with only 6.0 μL (1.0 M) K₂CO₃ is 1.36 ± 0.12 . The SRR is 1.30 ± 0.12 for IAC's impregnated with 2.0 μL H₂O and 6.0 μL (1.0 M) K₂CO₃. Our results are lower than the value of 1.9 ± 0.1 reported in Ref. [32]. These initial gravimetric studies involving 10 mg IAC samples of ZnCl₂ or K₂CO₃-impregnated

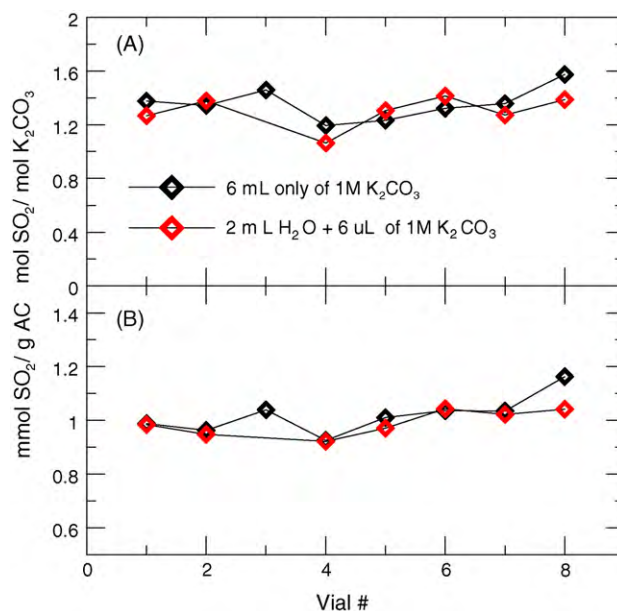


Fig. 7. A plot of the stoichiometric ratio of reaction (SRR) between SO₂ and K₂CO₃ with respect to sample replicates is shown in panel A. The calculated SRR's for these experiments were 1.36 ± 0.12 when impregnated with 6.0 μL (1.0 M) K₂CO₃ or 1.30 ± 0.12 when the samples are impregnated with 2.0 μL H₂O and 6.0 μL (1.0 M) K₂CO₃. A plot of the SO₂ capacities of these impregnated GC's is shown in panel B.

IAC's suggest that this method can be used for combinatorial screening.

3.4. Method validation using Cu(NO₃)₂ and H₃PO₄(MoO₃)₁₂ impregnated carbon (CuO IAC's)

The method was further validated by comparing the activity of bulk-prepared samples against the combi-prepared samples of a previously well-studied copper-impregnated activated carbon [14]. The use of the combi robot dictated that the two solutions were added sequentially. This procedure is different from bulk impregnations of these two impregnants wherein all components, including some HNO₃, of the impregnating solution were pre-mixed before adding to a previously dried activated carbon sample. Therefore it is important to determine if the sequential addition of impregnating solutions affects the material's ability to adsorb SO₂. In order to avoid potential damage to the robot, we decided to pre-treat the carbon with nitric acid (as described in Section 2.3) instead of including a nitric acid dispense. The use of HNO₃-treated GC for this study ensured even dispersion of the impregnants on the surface of the activated carbon generating nanoscale-sized impregnants as shown from previous studies [14,36]. HNO₃-treated GC was also found to aid in the adsorption of NH₃ [14,37]. Reports have also been made about the enhanced SO₂ adsorption onto activated carbon at low temperatures with HNO₃ treatment [38]. However, the exact mechanism of how HNO₃ treatment affects the binding of the impregnants with the activated carbon substrate is not yet fully understood and is currently being studied. It was also reported that IAC's containing CuO and H₃PO₄(MoO₃)₁₂·25 H₂O are efficient adsorbers of both SO₂ and HCN gases [14].

To study the effects of a sequential imbibe in the combinatorial samples, two sets of samples were impregnated using a different sequence of imbibes. The first set of samples received Cu(NO₃)₂·2.5 H₂O first followed by H₃PO₄(MoO₃)₁₂·25 H₂O, the second set was impregnated in the reverse order with H₃PO₄(MoO₃)₁₂·25 H₂O being dispensed first followed by Cu(NO₃)₂·2.5 H₂O. Both sets of samples were given an additional volume of de-aerated distilled

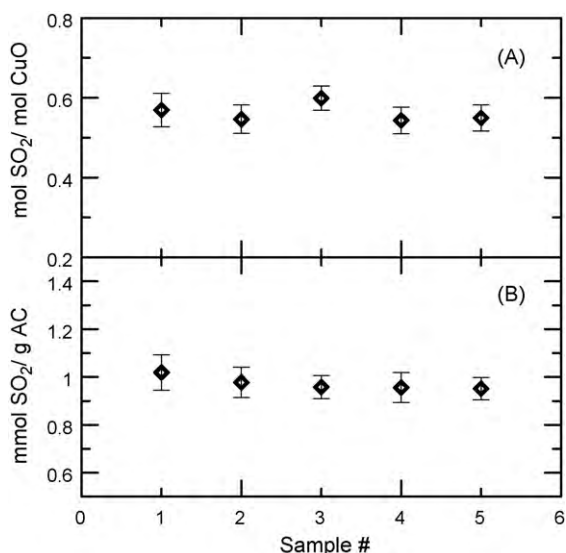


Fig. 8. Comparison plots showing the average stoichiometric ratio of reaction (SRR) (mol SO₂/mol CuO) of SO₂ with respect to CuO is shown in panel A. The average SO₂ capacity (mmol SO₂/g GC) is shown in panel B. The bulk sequentially impregnated samples of Cu(NO₃)₂ and PMA (Sample # 1); PMA and Cu(NO₃)₂ impregnated samples (Sample # 2) and bulk-prepared published multi-gas IAC (Sample # 3) are compared against the combinatorially prepared sequentially impregnated samples of Cu(NO₃)₂ and PMA (Sample # 4) and PMA and Cu(NO₃)₂ impregnated samples (Sample # 5). A summary of impregnation methods is shown in Table 1.

water to ensure that each grain of carbon in the sample is brought to the full imbibing limit of 8 μL/mg. After a full drying cycle, the impregnants were found to be well dehydrated and Cu(NO₃)₂ was fully decomposed to CuO as monitored by XRD.

The samples, when exposed to SO₂ challenge gas are thought to chemisorb to form copper sulfite (CuSO₃).



The mechanism for the formation of copper sulfate (CuSO₄) from CuSO₃ as observed in the soaking studies (Section 2.8) is not fully understood at this time and will require further studies. The adsorption of SO₂ by the robot-prepared materials was compared to similar amounts of bulk-prepared IAC's as shown in Fig. 8.

The SRR (SO₂ to CuO ratio) values (Fig. 8A) calculated for all the bulk and robot-prepared sequentially imbibed samples were about 0.55 ± 0.01. These values were averaged over sample sets containing eight replicates. This suggests that the order of impregnant addition during the sequential imbibe does not affect the adsorption capacity of the CuO IAC's. The plot of the adsorption capacity (Fig. 8B) of these samples showed that all gave similar results within error. The results in Fig. 8 further suggest that the combinatorial method of preparation of IAC's is comparable to the traditional method of making samples.

3.5. Combinatorial experiment with Cu(NO₃)₂·2H₂O and H₃PO₄(MoO₃)₁₂·25 H₂O

In the experiment described in Section 2.3.3, different combinations of Cu(NO₃)₂ and PMA IAC's were prepared and exposed to SO₂ gas. In the graph shown in Fig. 9, the SRR (SO₂ to CuO ratio) and the adsorption capacity (mmol SO₂/g carbon) was plotted versus the amount of Cu(NO₃)₂ initially imbibed. Fig. 9A shows that in all three replicate runs, the SRR values decreased with more CuO impregnant present. Fig. 9B shows that the SO₂ capacity increases as more Cu(NO₃)₂ (converts to CuO) was added. The average SRR calculated for replicates of the IAC impregnated with 1.75 × 10⁻² mmol CuO and 3.00 × 10⁻⁴ mmol PMA is 0.54 ± 0.01. This value is almost the

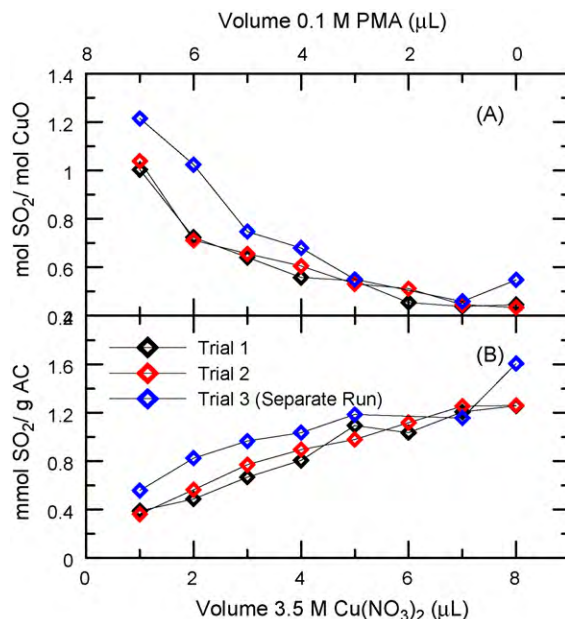


Fig. 9. Panel A shows the stoichiometric ratio of reaction (SRR) (mol SO₂/mol CuO) of SO₂ with respect to CuO and the SO₂ capacity (mmol SO₂/g GC) is shown in panel B of the 1-dimensional combinatorial experiment prepared by the sequential addition of 1, 2, 3, 4, 5, 6, 7, 8 μL Cu(NO₃)₂ with 7, 6, 5, 4, 3, 2, 1 μL PMA. A decreasing trend in the calculated SRR is observed in all three replicates as we increase the amount of Cu(NO₃)₂ in the impregnated carbon samples.

same as the SRR = 0.60, obtained for the bulk-prepared published recipe (Sample # 3) [14].

3.6. 2-Dimensional (2-D) combinatorial synthesis of Cu(NO₃)₂, Zn(NO₃)₂ and H₃PO₄(MoO₃)₁₂-impregnated activated carbons

Metal oxide impregnated samples of varying composition were used to evaluate the combinatorial approach for screening multi-gas adsorbent materials. An 8 × 8 array of CuO and ZnO IAC's containing different proportions of metal oxides was combinatorially prepared by adding increasing amounts of Zn(NO₃)₂ (x-direction) and Cu(NO₃)₂ (y-direction) in two dimensions onto HNO₃-treated GC's using the method described in Section 2.3 and in Fig. 2. The initial heating step at 200 °C (Section 2.7) decomposes the metal nitrates to the corresponding metal oxides. The CuO and ZnO IAC materials were evaluated gravimetrically for their ability to adsorb SO₂ gas when exposed for 4 h. Presumably, the metal oxides chemisorb SO₂ by reacting to form both copper and zinc sulfites which increases the sample mass. Fig. 10A shows a clear trend in SO₂ adsorption as the amounts of the impregnating solutions added to the prepared IAC's were varied. In general, the absorption capacity increases as the amounts of both Cu and Zn impregnants increase. This indicated that the more metal oxide impregnant present in these materials, the better they are for the removal of the toxic SO₂ gas. However, with an increase in the adsorption capacity of these materials, the SRR decreased showing that the effectiveness per molecule of impregnant decreases with loading as has been previously observed [14].

A group of 1-dimensional plots with respect to individual components for the experiments described in Fig. 10 are presented in Figs. 11 and 12. The dependence of the SO₂ gas adsorption on impregnant amount can be clearly discerned in Fig. 11. Fig. 11A shows the decrease in SRR with respect to increasing amounts of Zn(NO₃)₂, moving left to right. Fig. 11A also shows that the SRR decreases with increasing amounts of added Cu(NO₃)₂ going from top to bottom. Fig. 11C shows similar trends when plots are made with respect to increasing amounts of Cu(NO₃)₂. The 2-dimensional

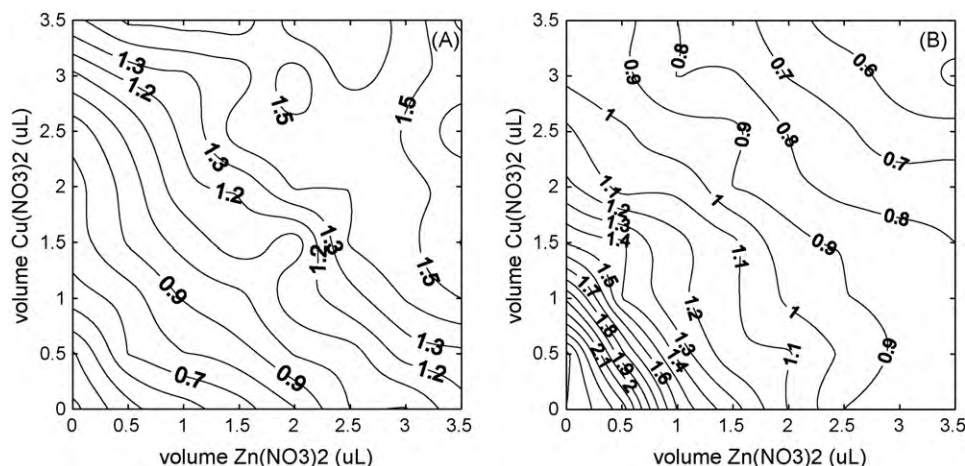


Fig. 10. 2-Dimensional plots of the (A) SO₂ capacity (mmol SO₂/g GC) and (B) stoichiometric ratio of reaction (SRR) (mol SO₂/mol CuO + mol ZnO) of the combinatorially prepared 8 × 8 array of CuO and ZnO impregnated activated carbon.

dependence of the SO₂ adsorption capacity on both components is very well represented in Fig. 11B and D. The results clearly indicate that multi-gas adsorbent materials can be prepared using the combinatorial method and evaluated for gas sorption by gravimetry.

Typically HNO₃ treatment is responsible for the NH₃ adsorption ability of these materials. Since a constant amount of HNO₃ was used to treat the material, one would expect the absence of a trend relating the NH₃ adsorption capacity with the amount of impregnant added. This was not the case for these materials. In Fig. 12A, we observe the dependence of NH₃ adsorption on increasing amounts of Zn present in the impregnant. This trend was presumed to be due to the amphoteric nature of ZnO. Consequently, no trend was observed in the NH₃ adsorption capacity of the materials when plotted against the amount of Cu added (Fig. 12 B). Clearly, the

presence of the ZnO impregnant functioned to improve the ability of these materials to adsorb NH₃ gas. No SRR's were calculated since the exact mechanism of NH₃ adsorption is not clearly understood and would require further studies.

3.7. Analysis of exposed IAC samples by TGA and powder XRD and confirmation of gas adsorption from soaking studies

Exposed and unexposed samples of CuO and ZnO IAC were analyzed by TGA. Exposed samples can be distinguished from unexposed samples by differences in the rate of change of mass with temperature in the 300–500 °C region (data not shown). The reason behind these differences is not fully understood at this time and will require further studies.

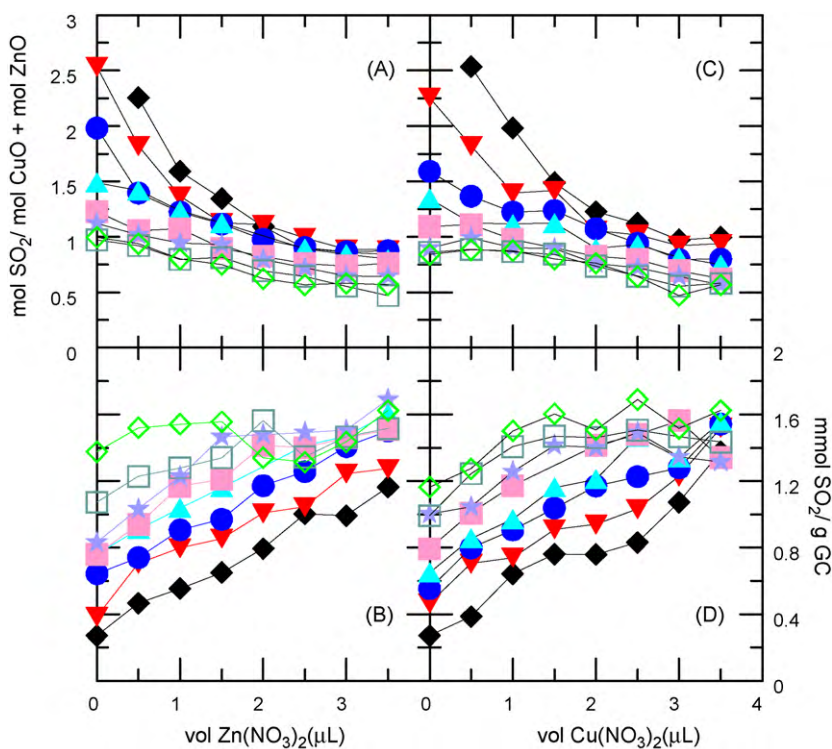


Fig. 11. Plots of (A) SRR (mol SO₂/mol CuO + mol ZnO) with respect to Zn(NO₃)₂, (B) SO₂ adsorption capacity (mmol SO₂/g GC) with respect to Zn(NO₃)₂, (C) SRR (mol SO₂/mol CuO + mol ZnO) with respect to Cu(NO₃)₂ and (D) SO₂ adsorption capacity (mmol SO₂/g GC) with respect to Cu(NO₃)₂. Individual curves in the graphs are plotted according to the specific volume of the second component added. Legend: (◆) 0.0 μL, (▼) 0.5 μL, (●) 1.0 μL, (▲) 1.5 μL, (■) 2.0 μL, (★) 2.5 μL, (□) 3.0 μL, (◇) 3.5 μL of either Cu(NO₃)₂ (in graphs A and B) or Zn(NO₃)₂ (in graphs C and D).

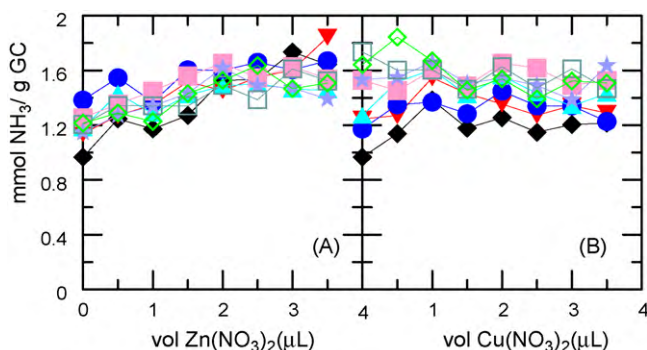


Fig. 12. Plots of NH_3 adsorption capacity ($\text{mmol NH}_3/\text{g GC}$) of the IAC's with respect to (A) $\text{Zn}(\text{NO}_3)_2$ and (B) $\text{Cu}(\text{NO}_3)_2$. Individual curves in the graphs are plotted according to the specific volume of the second component added. Legend: (◆) 0.0 μL , (▼) 0.5 μL , (●) 1.0 μL , (▲) 1.5 μL , (◻) 2.0 μL , (☆) 2.5 μL , (◻) 3.0 μL , (◇) 3.5 μL of either $\text{Cu}(\text{NO}_3)_2$ (in graph A) or $\text{Zn}(\text{NO}_3)_2$ (in graph B).

The unexposed control samples when analyzed by powder XRD, showed the broad humps at $2\theta = 25^\circ$ and $2\theta = 43^\circ$ for carbon as well as two sharper peaks with low intensities at $2\theta = 35.6^\circ$ and $2\theta = 38.9^\circ$ that match the two most intense peaks in the diffraction pattern of CuO. Both the XRD and TGA results for the unexposed control samples indicated that the metal nitrate impregnants were fully decomposed to their oxides after the heating cycle.

Powder XRD of SO_2 -exposed CuO and ZnO IAC's do not show sharp diffraction peaks except for broad humps at $2\theta = 25^\circ$ and $2\theta = 43^\circ$ characteristic of disordered carbon. This is expected since the impregnants should be fully dispersed with sizes that are in the nanometer range and therefore will not show sharp diffraction peaks in the XRD pattern [14].

When the SO_2 -exposed impregnated samples were soaked in water and the liquid recovered by filtering, CuSO_4 and ZnSO_4 salts (identified by XRD) were obtained upon drying the filtrate. These products prove that SO_2 was captured by the adsorbent. Presumably, the sulfite converted to the sulfates during the 10-day water exposure.

4. Conclusions

Activated carbon samples with varying amounts of several impregnants were successfully prepared *via* the combinatorial approach. These materials were analyzed by the gravimetric method resulting in a faster rate for screening of potential multi-gas adsorbents. The calculated adsorption capacities and stoichiometric ratios of reaction for known gas adsorbent materials such as ZnCl_2 IAC's as well as the K_2CO_3 IAC's, when evaluated using the combinatorial approach, were comparable to the values obtained from bulk samples using traditional methods of analysis.

By studying the SO_2 adsorption of CuO-impregnated carbon materials we were able to compare the SRR's of the combinatorially prepared samples with the ratios of traditionally prepared samples. The calculated values obtained from the combinatorial method were comparable to the bulk-prepared CuO samples.

Trends in gas adsorption capacities as well as in the stoichiometric ratio of reaction can be observed when analyzing samples with varying compositions. The mass increase of the samples after exposure to the challenge gas has been confirmed to be caused by the chemisorption reaction and not moisture uptake. The preliminary result obtained with the 2-D combinatorial experiment indicates that this method of sample preparation and analysis can effectively screen for viable multi-gas adsorbent materials. It is our goal to use this new method to rapidly screen for new combinations of impregnants that are suitable for adsorbing wide varieties of challenge gases.

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