防毒マスクの除毒能力試験に使用する四塩化炭素の代替物質に関する調査研究報告書

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防毒マスクの除毒能力試験に使用する四塩化炭素の代替物質に関する調査研究　報告書

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研究の目的

平成4年11月に開催されたモントリオール議定書第4回締約国会議の結果を受け、わが国はオゾン層保護を目的とする特定フロン等対策として「特定物質の規制等によるオゾン層の保護に関する法律」の改正などで対応することとしている。この関連で四塩化炭素は平成7年12月31日までに生産及び使用を全廃されることとなっている。一方、産業用防毒マスクの性能を規定する「防毒マスクの規格」においては、有機ガス用防毒マスクの除毒能力の試験ガスとして四塩化炭素を用いることが指示されており、従来はこの規格に従って有機ガス用防毒マスクの国家検定試験を行ってきた。これは過去において四塩化炭素が使用量及び使用頻度の高い代表的な有機溶剤であったことに由来している。

本研究所は防毒マスクの国家検定試験を担当していることから、上記の「オゾン層保護法」の施行に対応するために、産業用防毒マスクとして最も消費の多い有機ガス用防毒マスクの国家試験のために、四塩化炭素に替わる試験ガスを用いて行う試験方法を緊急に開発する必要がある。そのために、産業界で消費される代表的な有機溶剤の中から、オゾン層を破壊する虞れがなく、有機ガス用防毒マスクの性能を従来通り保証する試験に適した有機溶剤を選択し、その蒸気を用いて行う防毒マスクの試験条件を確立することが本調査研究の目的である。本調査研究の成果は、「防毒マスクの規格」改正の技術的基礎として資するものである。

研究の概要

本研究は情報調査と実験的研究によって行った。

第1部　情報調査

① 四塩化炭素の代替物質として検討対象となる範囲の有機化合物の生産方法、主な用途、生産量

② 上記の有機化合物の基礎的物性と有害性指標

③ 活性炭の有機溶剤蒸気に対する吸着特性

④ 諸外国の防毒マスク規格関係における「オゾン層保護法」への対応についての情報収集

⑤ 国家検定を既に合格した市販の有機ガス用吸収缶の寸法と活性炭充填量の調査。

第2部　実験的研究

代表的な市販の有機ガス用吸収缶について数種類の有機溶剤蒸気を試験ガスとした除毒能力試験を行い、四塩化炭素による試験結果に相応する結果を与える条件を検討した。具体的な研究の手順は次のようである。

① 防毒マスクの規格に合致した吸収缶試験条件で試験を刷ための吸収缶試験装置の構築。

② 市販の有機ガス用吸収缶の中から選んだ隔離式、直結式、直結式小型の各種吸収缶の有機溶剤蒸気を含む試験気流に対する破過曲線の測定。

③ 四塩化炭素によって試験した場合の除毒能力と等価の除毒能力を示すことができる新しい試験条件(ガスの種類、濃度）の確立。

結果

第1部　情報調査

①　検討対象範囲の有機化合物の市場性（生産方法、主な用途、生産量）

四塩化炭素の代替物質となる可能性のある有機化合物を7種類選択し、それらの工業的な生産と消費の概略、生産量を調査した結果を表1に示す。これらの物質は沸点、蒸気圧などが四塩化炭素に近く、かつ有害性や発ガン性が高くないこと、水溶性や化学反応性などが低く安定した物質であることを理由として選択した。

表1 有機化合物の生産方法、主な用途及び生産量　(参照資料1)

有機化合物の種類	主な生産法	主な用途	生産量(ton/年)
四塩化炭素	メタン塩素化、 二硫化炭素塩素化、 他	フロンガス原料、機械器具洗浄、不燃性溶剤、変圧器スイッチ油、ホスゲン原料	50,547 (平成2年) 53,171 (平成5年)
トリクロロエチレン	エチレン塩素化	金属機械洗浄、溶剤（生ゴム、染料、油脂等）、殺虫剤、抽出剤	56,850 (平成2年) 68,416 (平成5年)
ペンタン	石油精製の副生物、 分解ガソリン、 ナフサから抽出		石油化学工業会で把握していない。
ヘキサン	石油精製の副生物、 分解ガソリン、 ナフサから抽出	食用油抽出、 接着剤、塗料、インキなどの溶剤	石油化学工業会で把握していない。
ヘプタン	石油精製の副生物、 分解ガソリン、 ナフサから抽出		石油化学工業会で把握していない。
シクロヘキサン	石油留分、 ベンゼン水素化	カプロラクタム及びアジピン酸原料、有機溶剤（セルロ-ス、レジン、ワックス、油脂等）、剥離剤	629,449 (平成2年) 632,634 (平成5年)
トルエン	石炭タ-ル、 ナフサ分解	染料、香料、火薬、有機顔料、甘味料、テレフタル酸、医薬品等原料、溶剤、ベンゼン、キシレン原料	1,110,517 (平成2年) 1,219,515 (平成5年)

② 有機化合物の基礎的物性と有害性指標

上記の7 種類の有機化合物について基礎的物性及び有害性について調査した結果を表 2に示す。これらの物質は試薬としての入手が可能である。(参照資料 2～7)

表 2　有機化合物の基礎的物性と有害性指標としての管理濃度及び曝露限界濃度

有機化合物の種類	分子量	沸点 ℃	蒸気圧 25℃	水溶性 水中へ25℃	管理濃度 ppm	許容濃度 ppm	TLVs ppm
四塩化炭素	151.82	76.64	115.2mmHg	0.077wt%	5	5 皮	5,A3,Skin
トリクロロエチレン	131.39	87.19	47.3mmHg	0.137wt	50	50	50,A5
ペンタン	72.15	36.07	512.5mmHg	0.0038wt%		300	600
ヘキサン	86.74	68.74	151.3mmHg	0.00123wt%	50	40 皮	50
ヘプタン	100.20	98.42	45.7mmHg	0.000357wt%		200	400
シクロヘキサン	84.16	80.73	97.8mmHg	0.010wt%		150	300
トルエン	92.14	110.63	28.5mmHg	0.0515wt%	50	50(暫定)	50,Skin

③　活性炭の有機溶剤蒸気吸着特性の文献的調査 (参照資料　8～10)

有機ガス用吸収缶に活性炭を除害剤として充填していることは各国共通である。有機ガス用吸収缶の各種有機化合物蒸気に対する除毒能力は活性炭の性質と充填量、充填の形状によって決まるものと考えることができる。G.O.Nelson等は一定量の活性炭を実験的に充填した吸収缶モデルに対して121種類の有機化合物蒸気(ただし濃度は1000ppm)を含む試験気流(相対湿度50%)を通気した時の破過時間を報告したが、それによれば四塩化炭素の破過時間に近い破過時間を与える物質として1-クロロヘキサン、クロロシクロペンタン、酢酸プロピル、酢酸ブチル、2-ブタノン、ヘプタン、ノナンなどが挙げられる。その他にも2-エトキシエタノ-ルなどの親水性化合物も挙げられるが、このような物質の蒸気が活性炭に吸着する場合には空気中の水蒸気の影響が吸着特性に特異的に現れる性質があり、一般の有機化合物の吸着を正しく代表するものではないことから、考慮の対象としなかった。

田中　茂らは、市販の有機ガス用直結式小型吸収缶を用いて40種類の有機化合物蒸機(ただし濃度は300ppm)を通気したときの破過時間を測定したが、その結果では四塩化炭素の破過時間に近い破過時間を与える物質としてトリクロロエタン、酢酸エチル、酢酸ブチルが挙げられる。この中で四塩化炭素に性質の近いトリクロロエタンが注目されるが、この物質は四塩化炭素と同様にオゾン層保護のための規制対象であるために本研究の目的物質とならない。表2に示す諸物性と規制などの社会的背景からの判断として、室温での蒸気圧が四塩化炭素に近いものとしてシクロヘキサン、ヘキサンを、水溶性が四塩化炭素に近いものとしてシクロヘキサン、トリクロロエチレン、トルエンを挙げることができる。

活性炭充填層の除毒能力を試験する目的から考えると、吸収缶が吸湿等により性能劣化する程度を正確に検出することが必要であり、そのために四塩化炭素の代替化合物は水溶

性の程度も四塩化炭素に近いことが望まれる。

④　諸外国の防毒マスク規格関係における「オゾン層保護法」への対応

有機ガス用防毒マスク吸収缶の四塩化炭素による従来の試験条件と、四塩化炭素の代替物質についての諸外国の対応は次のようである。

1) 米国 (参照資料11～14)

米国では呼吸保護具の国家検定試験に関する規格として20年以上に亘って Title 30 CFR Part 11 -Respiratory Protective Devices; Test for Permissibility; Fees (June 28, 1974) (参照資料11)があり、これの改正案として Title 42 CFR Part 84 - Respiratory Protective Devices (Proposed Rules, May 24, 1994) (参照資料 12)が提案されている。この改正は粒子状物質に対するフィルターろ過効率の測定法と基準を改正したもので防毒マスク吸収缶の試験条件は変化していない。Title42 CFR 84, Part 11 - Subpart I の試験条件は表 3及び4のようである。

表 3　防毒マスクの有機ガス用吸収缶の除毒能力試験条件と所要破過時間(Subpart I)

破過時間の測定は透過濃度 5ppm の時としている。

種類	吸収缶の条件	試験条件	除毒能力
Front mounted or back mounted with full facepiece (隔離式吸収缶)	As received	64L/min, 25 ℃, 50% RH, CCl_4 2%	12 分(3個)
	Equilibrated at 25% RH for 6hr	64L/min, 25 ℃, 50% RH, CCl_4 2%	12 分(2個)
	Equilibrated at 85% RH for 6hr	64L/min, 25 ℃, 50% RH, CCl_4 2%	12 分(2個)
Chin-style gas mask (直結式吸収缶)	As received	64L/min, 25 ℃, 50% RH, CCl_4 5,000ppm	12 分(3個)
	Equilibrated at 25% RH for 6hr	64L/min, 25 ℃, 50% RH, CCl_4 5,000ppm	12 分(2個)
	Equilibrated at 85% RH for 6hr	64L/min, 25 ℃, 50% RH, CCl_4 5,000ppm	12 分(2個)
Escape gas mask with facepiece or mouthpiece (避難用吸収缶)	As received	64L/min, 25 ℃, 50% RH, CCl_4 5,000ppm	12 分(3個)
	Equilibrated at 25% RH for 6hr	64L/min, 25 ℃, 50% RH, CCl_4 5,000ppm	12 分(2個)
	Equilibrated at 85% RH for 6hr	64L/min, 25 ℃, 50% RH, CCl_4 5,000ppm	12 分(2個)

表４　有機ガス用Cartridge(直結式小型吸収缶)の除毒能力試験条件(Subpart L)
破過時間の測定は透過濃度 5ppm の時としている。

種類	吸収缶の条件	試験条件	除毒能力
Chemical cartridge respirator (直結式小型吸収缶)	As received	64L/min, 25 ℃, 50% RH CCl_4 1,000ppm	50 分(3個)
	Equilibrated at 25% RH for 6hr	64L/min, 25 ℃, 50% RH CCl_4 1,000ppm	50 分(2個)
	Equilibrated at 85% RH for 6hr	64L/min, 25 ℃, 50% RH CCl_4 1,000ppm	50 分(2個)

四塩化炭素の代替物についてのレポ-トとして E.S.Moyer, J.A.Peterson and C.Calvert による NIOSH File Report, Evaluation of Carbon Tetrachloride Replacement Agents for Testing Organic Vapor Cartridges その他の2報が公表されている(参照資料13)。この研究では隔離式、直結式及び直結式小型(chemical cartridge)の各4種類の市販銘柄について、酢酸エチル、ペンタン、n-ヘキサン、ヘプタンを四塩化炭素と比較し、ペンタンを選んだ。この実験は温度(25℃)、相対湿度(50%)の空気流(64L/min)に四塩化炭素1000ppm を含む試験気流で試験したときに測定される破過時間と同じ破過時間を与える物質とその濃度を決めることを目的として計画された。また、試験ガスの有害性が低いこと、非水溶性であること、取扱いの安全性、蒸気濃度の測定が容易であることも考慮したとしている。試験ガス濃度を4段階に設定して吸収缶に導入した時の出口濃度の時間経過を定し、出口濃度が5ppmとなった時を破過時間として、破過時間と試験ガス濃度の関係(破過曲線図)を求めている。

以上の結果から、代替候補物質はいずれも試験濃度を調節することにより四塩化炭素による破過時間と同じ破過時間を与える条件を見いだせるが、n-ヘキサンは有害性が強いこと、酢酸エチルは水溶性が高いこと、ヘプタンは試験ガスを高い濃度とする必要があることを理由としてペンタンを代替物質として選定した。

この実験では試験ガスの発生にシリンジポンプを使用して液体を連続的に気化する方法を採用しており、濃度変動を平均化するためにバッファタンクを使用している。試験ガスと漏洩ガスの濃度モニタ-には Miran 1A (Infrared Gas Analyzer) を使用している。

この実験の結果に基づいて、NIOSHは防毒マスクメーカーに対して次のような指示を示している。(参照資料14)　直結式小型吸収缶については As received 状態の吸収缶について、気流の試験条件としては温度25℃、相対湿度50%でペンタン濃度1000ppmを含む試験気流(64 L／分)に対して破過時間50分以上としている。しかし四塩化炭素代替物としてペンタンに限定していない。メーカーは他の化学物質でも、四塩化炭素で測定した破過時間と等価な破過時間を測定できる条件が設定できることを示せば、その試験条件を認めるとしている。

同様に直結式吸収缶に対しては温度25℃、相対湿度80%でペンタン濃度4000ppmを含む

試験気流(64 L／分)で測定することとし、破過時間27分以上としている。この場合も四塩化炭素代替物はペンタンに限らないとしている。

隔離式吸収缶に対しては温度25℃、相対湿度80%でペンタン濃度10, 000ppmを含む試験気流(64 L／分)に対して破過時間50分以上としている。この場合も四塩化炭素代替物はペンタンに限らないとしている。

従来の米国の試験条件では検定試験品として受け入れた吸収缶を、試験の前に相対湿度25%と85%の気流中にそれぞれ6時間保ち、前処理をした後に相対湿度50%の試験気流で破過時間を測定する試験があったが、新しい試験条件では前処理をせずに、受け入れた状態のままの試験品について相対湿度50%または80%の試験気流を用いた試験だけとしている。その理由として前処理が必ずしも厳しい試験ではなかったこと、前処理に時間が係ったこと、試験気流自体を相対湿度80%にすることが最も破過時間を短縮する条件であることを確認したためであるとしている。

2) カナダ (参照資料 15)

カナダは米国の規格に従う方針であるが、オンタリオ州のメ-カ-であるRacal Filter Technologies, Ltd. のS.J.Smith氏からの私信によれば四塩化炭素の代替物質として米国が挙げているペンタンは沸点が36℃と低いために精確な取扱いが難しいこと、NIOSH のDr.Moyer等によるデ-タは対数表示で微少な差がはっきり読みとれないこと、n-ヘキサンが最も近い破過時間を示していること、酢酸エチルの破過時間もそれほど大きい差はないこと、などを挙げてペンタンの採用に疑問を呈している。

3) ヨ-ロッパ (資料 16、17参照)

ヨ-ロッパ連合(EU)では防毒マスクの規格としてEN141(August 1990)が有効である。この規格では有機ガス用の吸収缶の区分と除毒能力試験条件を表 5のように定めている。
四塩化炭素の代替物質について、英国のメ-カ-であるThe Associated Octel Company Limited の Dr. P. Malloy 氏の International Society for Respiratory Protection (April 21, 1994) における発表情報によれば、CEN TC79 SC4 では種々の試験結果を集めて検討した結果、四塩化炭素の代替物としてシクロヘキサンと 2-ブタノンが最も目的に近い物質であるということとなり、さらに研究所間で比較試験を行った。その後の私信によれば、ヨ-ロッパでは既にシクロヘキサンを四塩化炭素の代替物と決めた。この決定はChiswickで開催されたCEN Standard meeting で合意された。その試験条件は表 6の通りである。EN141 は1995年に改正される予定であり、その改正にこの決定が含まれる予定である。

表 5　EN141(August 1990)における有機ガス(Type A: 沸点65℃以上の有機ガス対象)用の区分と除毒能力試験条件(Subpart I)

種類	吸収缶の条件	試験条件	除毒能力
Class 1 Low capacity	After the tests of mechanical strength and breathing resistance	30L/min, 20 ℃, 70% RH CCl_4 1,000ppm	80分(3個) 15.4g 以上の重量増加
Class 2 Medium capacity	After the tests of mechanical strength and breathing resistance	30L/min, 20 ℃, 70% RH CCl_4 5,000ppm	40 分(3個) 38.4g以上の重量増加
Class 3 High capacity	After the tests of mechanical strength and breathing resistance	30L/min, 20 ℃, 70% RH CCl_4 1%	60 分(3個) 115.2g以上の重量増加

ただし除毒能力は試験条件の欄に示された試験気流を導入したときに、試験ガスの出口濃度が5ppmに達するまでの間に吸収される四塩化炭素によって起きる重量増化の値によって示されている。

表 6　EN141 における四塩化炭素の代替試験ガス

試験ガス：シクロヘキサン		
フィルタ-の種類	試験ガス濃度	試験条件での最短破過時間
A1	0.1%	70分
A2	0.5%	35分
A3	0.8%	65分

4) オ-ストラリア (資料 18参照)

オ-ストラリアでは現在はEN141 に従って試験している。

オ-ストラリアのメ-カ-であるSafety Equipment Australia Pty Ltd. の G.Powe と G. Berndtsson 氏によれば、オ-ストラリア独自で四塩化炭素の代替物を決める努力はしていない。米国NIOSHとEUがそれぞれ努力していることは知っている。最初に代替物を決めた国の方針に従うだろう。

5) 韓国

労働省が行っている韓國勤労者職業病予防事業プロジェクト組織を通じて韓國産業安全公団産業安全研究院に問い合わせたところ次のような伝言を得た。「四塩化炭素を使用できなくなることは知っているが、実験的な検討はしていない。日本の結果を参照する。」ただし文書による回答はなかった。

⑤　国家検定に合格している有機ガス用吸収缶の寸法と活性炭充填量の調査

国内で流通している有機ガス用吸収缶のメ-カ-を対象に、それぞれの吸収缶の寸法、活性炭充填量についての調査を行った。これは、吸収缶の破過時間は活性炭充填量のみでなく充填層の形状によっても影響される可能性があるため、実験に用いる吸収缶を適当に選択するためである。調査結果を表7に示す。吸収缶の一般的な構造を冒頭に示す。

表7 (その1)　市販の有機ガス用吸収缶の寸法と活性炭充填量

型式名	区分	層の直径	層の高さ	活性炭充填量
KG-27	直結式小型	内側75.5～74.5mm	内側21mm	90～95mL 45～50g
1C	直結式小型	内側79.6mm	内側29.6mm	52g
3C	直結式小型	内側76.5mm	内側20.0mm	38g
5C	直結式小型	内側79.6mm	内側18.0mm	30g
6C	直結式小型	内側77.8mm	内側18.0mm	30g
7C	直結式小型	内側75.5mm	内側22.5mm	39g
8C	直結式小型	内側75.2mm	内側15.0mm	23g
10C	直結式小型	内側68.0mm	内側17.5mm	23g
16C	直結式小型	内側77.0mm	内側25.0mm	45g
直結	直結式	内側85.0mm	内側35.0mm	80g
隔離	隔離式	内側145.0mm×76.0mm	内側68.0mm	270g
G31	直結式小型	内側80mm	内側11mm	22g
G32	直結式小型	内側80mm	内側11mm	22g
G34	直結式小型	内側80mm	内側21mm	42g
G35	直結式小型	内側80mm	内側11mm	22g
G36	直結式小型	内側80mm	内側21mm	42g
直結式1型吸収缶C	直結式	内側85mm	内側35mm	80g
隔離式1型吸収缶M	隔離式	内側145mm×76mm	内側100mm	420g
隔離式1型吸収缶C	隔離式	内側145mm×76mm	内側68.0mm	270g

表 7 (その 2)　市販の有機ガス用吸収缶の寸法と活性炭充填量

型式名	区分	層の直径	層の高さ	活性炭充填量
CA-104N II	直結式小型	内側 77mm	内側20mm	41g
CA-104N II OV/AG	直結式小型	内側 77mm	内側21mm	47g
CA-104F	直結式小型	内側 77mm	内側19mm	40g
CA-107F OV	直結式小型	内側 77mm	内側15mm	33g
CA-1P2F	直結式小型	内側 78mm	内側 6mm	14g
CA-2P2F	直結式小型	内側 78mm	内側 6mm	14g
CA-1P8	直結式小型	内側 68mm	内側13mm	25g
CA-1P1	直結式小型	内側 68mm	内側21mm	29g
CA-1P1 OV	直結式小型	内側 68mm	内側19mm	31g
CA-108K	直結式小型	内側 68mm	内側13mm	22g
CA-408	直結式	内側105mm	内側35mm	131g
CA-604	直結式	内側95mm×84mm	内側35mm	101g
CA-604 OV	直結式	内側79mm	内側39mm	85g
CA-501	隔離式	内側13.5mm×75mm	内側114mm	312g
3M 6001	直結式小型	断面積 74 cm^2	内側18mm	50g
3M 6011	直結式小型	断面積 74 cm^2	内側18mm	50g
3M 4251	直結式小型	断面積 67 cm^2	内側15mm	50g
R100(B)-G56	直結式小型	外側67～70mm	外側 8mm+23mm	31.5±1.5g
RQ100(B)-G56		内側64～67mm	内側 6mm+21mm	
R101-G77	直結式小型	外側77.4mm	外側23.5mm	31.5±1.5g
		内側75mm	内側19.5mm	
G77II	直結式小型	外側77mm	外側24.5mm	31.5±1.5g
		内側74mm	内側21mm	

第2部　実験的研究

①　防毒マスクの規格に合致した吸収缶試験装置の構築。

有機ガス用防毒マスク吸収缶の破過時間を測定するための装置として、試験ガス流の発生装置、吸収缶を保持する恒温空気浴および吸収缶の出口ガス濃度の時間変化を連続的に測定するためのガスクロマトグラフを連結した装置を構築した。各部の性能は以下の通りである。

試験ガス流発生装置

主空気流発生：空気コンプレッサーから圧力調整装置を通して減圧して発生した空気流を1～4 気圧に圧力制御して発生し、その圧を保ったまま恒温水槽中でバブリングさせて水蒸気を飽和した後、同じ温度で1気圧に減圧することによって主気流の温度と湿度を制御した。恒温水槽の温度は20℃±0.1℃に制御し、恒温水槽内部の気圧を2気圧として水蒸気を飽和したとき、1気圧に減圧した後の空気流の相対湿度は50%に調整されている。恒温水槽内部の気圧を4気圧までの範囲で調整することによって最終的な試験気流の相対湿度を20%以上の任意の範囲に調整することができる。

試験ガス発生：試験ガスとする有機化合物を1Lの丸底フラスコに入れて恒温水槽で冷却または加温し、蒸気を発生した。この丸底フラスコの枝管から低流量の空気流を導入し、フラスコの上部に取り付けた還流装置を通して取り出した。還流温度をフラスコの温度より低く制御することによって、還流温度での飽和蒸気を含む安定な気流を得ることができた。この飽和蒸気を含む低流量の気流を主気流に混合した。

試験ガス流の温湿度と濃度の調整：試験ガス流の最終的な流量は30L／分となるように調節した。温度は20℃±0.1℃、相対湿度は50%と80%に調整した。試験ガスの濃度は隔離式吸収缶に対して3000～8000ppm、直結式吸収缶に対して1000～5000ppm、直結式小型吸収缶に対して100～600ppmの範囲とした。

試験ガス発生装置の構成を図 1 に示す。

破過時間の測定

恒温空気浴中に保った吸収缶に試験ガス流を導入した時の吸収缶出口ガスを細い配管でガスクロマトグラフ分析装置の自動サンプラーに導入し、約 3 分間隔で試験ガス漏洩濃度を測定して破過曲線を描いた。破過曲線上で、吸収缶に試験ガスの導入を始めた時間から漏洩ガス濃度が10ppmに達するまでの時間を破過時間とした。その他に漏洩ガス濃度が50ppmに達する時間、試験ガス濃度の50%に達する時間も測定した。被験吸収缶を設置した恒温空気浴の構造を図1-2に示す。この恒温空気浴の内部には2個の吸収缶を設置するアダプターがあり、1個の吸収缶を試験している間に他の1個を恒温に保つことができる。1

個の破過時間の測定が終了した後には、流路の配管をバルブで切り替えて他の吸収缶の試験を開始する。

② 市販の有機ガス用吸収缶の中から選んだ隔離式、直結式、直結式小型の各種吸収缶の有機溶剤蒸気を含む試験気流に対する破過曲線の測定。

市販の吸収缶の中から本実験の対象として使用したものの形状を表 8 に示す。表 8 に示す吸収缶に試験ガスを導入して測定した破過曲線の例を図 2 ～ 図 8に示す。
図 2～5に示すように、本実験では同じロットの吸収缶について複数回測定した破過曲線が高い再現性を示すことが分かった。このようにして測定した破過曲線から読みとった破過時間を表 9 に示す。

表 8 実験対象とした吸収缶の種類と形状

種類	層の直径	層の高さ	活性炭充填量
隔離式A	内径135mm×75mm	内側114mm	312g
隔離式B	内径145mm×76mm	内側 68mm	270g
直結式B	内径85mm	内側 35mm	80g
直結式小型A	内径77mm	内側 20mm	41g
直結式小型B	内径75.2mm	内側 15mm	23g

③ 四塩化炭素による除毒能力試験と等価の除毒能力を示す試験条件

ガスの種類と濃度の確定

表 9 に示す破過時間を試験ガス濃度との関係でプロットした破過曲線図を図 9 ～図 16 に示す。これらの図は吸収缶の種類毎に、また試験ガスの相対湿度が50%か80%かによって区分して示した。

その結果、直結式小型吸収缶に対しては、四塩化炭素とシクロヘキサンの破過曲線は湿度が50%か80%かに係わらず互いに近い値を示した。湿度が高くなるにつれて破過時間が短縮する程度が四塩化炭素とシクロヘキサンでは同じであることもシクロヘキサンの利点と考えられる。

ヘプタンを試験ガスとした破過時間の測定値は数が少なかったが、いずれの測定値も四塩化炭素の破過曲線図上にほぼ位置した。

直結式吸収缶については1銘柄のみの測定となったが、相対湿度50%と80%の何れでもシクロヘキサンは四塩化炭素と殆ど同じ破過曲線図を示した。隔離式吸収缶2銘柄についてもシクロヘキサンと四塩化炭素の破過時間を測定した。2段階の相対湿度において、ど

表 9-1　直結式小型吸収缶の破過時間　四塩化炭素

吸収缶の種類	ガスの種類	濃度	温度	湿度	Bt10ppm	Bt50ppm	Bt50%
		ppm	℃	相対％	min	min	min
直結式小型A	CCl_4	150	20	50%	513	595	622
		150	20	50%	524	595	622
		150	20	50%	502	573	611
		150	20	50%	518	589	622
		300	20	50%	314	360	401
		300	20	50%	331	377	418
		600	20	50%	177	203	242
		600	20	50%	177	201	240
		300	20	50%	322	365	410
		150	20	83%	203	219	246
		150	20	84%	195	227	236
		150	20	83%	206	238	249
		300	20	80%	159	180	203
		300	20	80%	157	180	204
		300	20	86%	151	172	193
		600	20	80%	112	131	157
		600	20	80%	112	128	154
直結式小型B	CCl_4	150	20	51%	234	330	363
		150	20	51%	225	351	381
		300	20	53%	111	159	214
		300	20	52%	107	171	225
		600	20	52%	64	89	128
		600	20	52%	62	92	133
		150	20	82%	64	97	110
		150	20	86%	67	94	105
		300	20	86%	42	65	81
		300	20	82%	50	77	100
		600	20	85%	49	55	76
		600	20	85%	30	47	70

表 9-2　直結式小型吸収缶の破過時間　シクロヘキサン

吸収缶の種類	ガスの種類	濃度	温度	湿度	Bt10ppm	Bt50ppm	Bt50%
		ppm	℃	相対%	min	min	min
直結式小型A	Cyclohexane	127	20	52%	546	630	636
		127	20	50%	532	615	632
		254	20	50%	330	373	407
		254	20	53%	327	373	403
		254	20	51%	315	355	388
		508	20	53%	188	214	248
		508	20	50%	198	217	250
		127	20	83%	202	228	235
		127	20	81%	212	237	250
		127	20	82%	212	237	248
		254	20	81%	168	186	202
		254	20	85%	160	178	197
		254	20	85%	164	183	202
		508	20	86%	118	130	150
		508	20	83%	123	135	155
		508	20	87%	119	131	151
直結式小型B	Cyclohexane	127	20	52%	278	370	392
		127	20	52%	279	383	404
		254	20	52%	146	196	239
		254	20	52%	144	193	241
		508	20	52%	72	96	134
		508	20	53%	72	96	135
		127	20	86%	63	97	101
		127	20	84%	76	101	107
		254	20	83%	52	70	85
		254	20	82%	71	89	104
		508	20	82%	32	46	68
		508	20	82%	47	60	81

表 9-3　直結式小型吸収缶の破過時間　ヘプタン

吸収缶の種類	ガスの種類	濃度	温度	湿度	Bt10ppm	Bt50ppm	Bt50%
		ppm	℃	相対%	min	min	min
直結式小型B	Heptane	152	20	51%	228	358	384
		300	20	50%	135	171	204
		620	20	49%	58	75	102
		450	20	82%	63	85	130

表 9-4　直結式吸収缶の破過時間　四塩化炭素

吸収缶の種類	ガスの種類	濃度	温度	湿度	Bt10ppm	Bt50ppm	Bt50%
		ppm	℃	相対％	min	min	min
直結式B	CCl_4	1597	20	47%	118	129	182
		3088	20	46%	53	57	97
		5107	20	51%	41	44	64
		1614	20	80%	114	123	164
		3113	20	83%	58	63	97
		5122	20	80%	40	43	63

表 9-5　直結式吸収缶の破過時間　シクロヘキサン

吸収缶の種類	ガスの種類	濃度	温度	湿度	Bt10ppm	Bt50ppm	Bt50%
		ppm	℃	相対％	min	min	min
直結式B	Cyclohexane	1032	20	50%	154	172	238
		2982	20	50%	61	66	94
		1032	20	80%	133	143	183
		2985	20	80%	54	59	89

表 9-6 隔離式吸収缶の破過時間 四塩化炭素

吸収缶の種類	ガスの種類	濃度	温度	湿度	Bt10ppm	Bt50ppm	Bt50%
		ppm	℃	相対％	min	min	min
隔離式A	CCl_4	3090	20	50%	288	297	356
		4688	20	50%	194	201	243
		7713	20	50%	120	124	151
		2750	20	80%	279	291	347
		4599	20	80%	195	205	237
		7203	20	80%	117	122	149
隔離式B	CCl_4	1157	20	50%	645	692	836
		3112	20	47%	265	278	345
		5148	20	49%	148	160	212
		7362	20	50%	107	113	152
		1047	20	80%	475	540	693
		3068	20	80%	234	254	318
		5098	20	80%	154	162	209
		7210	20	80%	105	113	147

表 9-7 隔離式吸収缶の破過時間 シクロヘキサン

吸収缶の種類	ガスの種類	濃度	温度	湿度	Bt10ppm	Bt50ppm	Bt50%
		ppm	℃	相対％	min	min	min
隔離式A	Cyclohexane	3062	20	50%	268	277	340
		4566	20	50%	196	202	235
		6807	20	50%	132	137	164
		3043	20	80%	261	271	325
		4971	20	80%	172	183	209
		6635	20	80%	127	131	156
隔離式B	Cyclohexane	1090	20	50%	636	688	793
		3170	20	48%	226	242	302
		4959	20	50%	135	144	187
		6285	20	50%	115	122	161
		1019	20	80%	468	519	657
		2942	20	80%	206	221	290
		5066	20	80%	144	152	189
		6125	20	80%	105	113	163

ちらの試験ガスを用いても破過時間に殆ど差は見られなかった。また上記のいずれの吸収缶についても実測した破過時間は1本の破過曲線図上に高い相関係数で一致しており、測定のバラツキは小さかった。このことは破過時間の測定条件が安定しており、信頼性のある測定が行われたとことを示している。

4. 考察

本研究では四塩化炭素の代替物質としてシクロヘキサンを主として検討した。その理由の一つはシクロヘキサンの沸点が80.73℃で四塩化炭素の沸点に近く、試験ガスとして蒸発法で蒸気を発生する場合に、蒸気濃度を一定に調製するための蒸発装置と冷却装置の温度設定が室温に近い範囲となり、配管壁面での結露や、また室温による温度制御の妨害が少ない。このことは吸収缶試験条件の設定が容易であり、しかも安定で精度が高くなることを意味している。また曝露限界濃度勧告値としてのACGIHのTLVsまたは日本産業衛生学会の許容濃度が150ppmと高く、有害性が低いと考えられること、水との相互溶解性が低い点で四塩化炭素に近い性質であることも重要な理由と考えた。ヘキサンの沸点も86.2℃で四塩化炭素に近い範囲にあるが、曝露限界濃度勧告値が50ppmmまたは40ppmと低く、それだけ有害性が強いと考えたためである。

シクロヘキサンの蒸気を試験ガスとして毎分30Lの気流中に100ppm～5000ppmの濃度で発生するためには、蒸発器の温度を10℃～30℃に保つことで目的を達する。四塩化炭素の沸点は76.6℃であり、従来、四塩化炭素の蒸発条件はほぼ同じであった。一方、米国NIOSHが推薦しているペンタンは沸点が36.1℃であり、この蒸気を安定に発生するためには0℃以下の温度で蒸発をさせる必要が生じる。この条件では配管の結露が起きるため装置の保守が困難になる。また冷却用に水を使用できない。ヘプタンは沸点が100.2℃であり、この蒸気を同じ濃度範囲で発生するためには蒸発器の温度を40℃～60℃に保つ必要が生じる。この温度で蒸発させた蒸気は配管の途中で室温で冷却されて凝縮する恐れがある。このような理由でシクロヘキサンは蒸気発生の温度管理が容易な溶剤である。

実際に国家検定に合格している有機ガス用の防毒マスク吸収缶について四塩化炭素とシクロヘキサンを含む試験気流で破過時間(漏洩ガス濃度が10ppmとなる時間とした)を測定したところ、直結式小型吸収缶、直結式吸収缶及び隔離式吸収缶の何れでもシクロヘキサンの破過時間－試験ガス濃度の関係曲線（破過曲線図）は四塩化炭素の破過曲線図と殆ど同じであった。2種類の試験ガスの破過時間の近似性は試験気流の相対湿度を50%から80%に変化させても変わらなかった。

このような結果から有機ガス用防毒マスク吸収缶の除毒能力試験の試験ガスとして、四塩化炭素の替わりにシクロヘキサンを使用することに特に問題はないと推測される。従来の有機ガス用吸収缶の四塩化炭素により測定される破過時間は規格に定める破過時間に比して余裕があることから、シクロヘキサンによる試験においても従来と同一の濃度条件で測定することとし、要求される破過時間値も従来と同じに設定して支障はないと考える。

5. 結論

シクロヘキサンとヘプタンの蒸気を試験ガスとして含む空気流は四塩化炭素を試験ガスとした時の各吸収缶の破過曲線図とほぼ同じ破過曲線を示すことが証明された。この2種類の物質を比較すると、蒸気発生の段階でヘプタンは室温より高い60℃程度の温度を必要とするために、蒸気発生装置の下流側で配管内にヘプタン蒸気が凝縮することがあり、蒸気の安定な発生に難点があることが分った。一方、シクロヘキサンの蒸気発生温度はほぼ室温と同じ30℃前後であったことから、試験ガスの濃度が安定していた。

このような装置の運転条件の優有性、同じ試験ガス濃度に対する破過時間が四塩化炭素とほぼ同じであること、試験ガスの湿度を高くした場合の破過時間の短縮の程度も四塩化炭素と同程度出あること、およびヨーロッパ諸国連合と同じ試験ガスであること、を考慮すると、シクロヘキサンは四塩化炭素の代替物質として推賞される。

シクロヘキサンを防毒マスク吸収缶の除毒能力の試験ガスとして使用する条件としては、表10に示すように、濃度と破過時間の最低要求値は四塩化炭素を試験ガスとした場合と同じでよいと考える。

表 10 四塩化炭素とシクロヘキサンの等価な試験条件(試験ガス濃度、破過時間)

	直結式小型	直結式	隔離式
四塩化炭素	300ppm, 50分	3,000ppm, 30分	5,000ppm 100分
シクロヘキサン	300ppm, 50分	3,000ppm, 30分	5,000ppm 100分

参考資料

(1) 化学工業日報社、11892の化学商品、東京 (1992) 及び12695の化学商品、東京 (1995)

(2) J.A.Riddick, W.B.Bunger and T.K.Sakano, Organic Solvents, 4th Edition, Wiley Interscience, New York (1986)

(3) Edited by S.Budavari et al, The Merck Index, 11th Edition, Merck & Co., Inc. , (1989)

(4) 井上　俊　他、わが国における工業用有機溶剤使用の実態に関する調査研究、産業医学　26巻、518p (1984)

(5) 関東化学㈱　総合カタログ No.18　(1994)

(6) American Conference of Governmental Industrial Hygienists、1994-1995 & 1995-1996 Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices (1994 & 1995)

(7) 日本産業衛生学会、許容濃度等の勧告、産業医学 36巻、236 (1994 & 1995)

(8) 松村芳美、防毒マスク、労働衛生工学　19巻 25 (1980)

(9) G.O.Nelson and C.A.Harder, Respirator Cartridge Efficiency Studies: V. Effect of Solvent Vapors, Amer. Ind. Hygiene Assoc. J. Vol.35, 391 (1974) または　Amer. Ind. Hygiene Assoc. Monograph Series, Respiratory Protection, 234 (1985)

(10) 田中　茂、有機溶剤上記46種類に対する有機ガス用吸収缶の破過時間、産業医学 35巻 290 (1993)

(11) Title 30, CFR Part 11, Respiratory Protective Devices (1974),
Subpart I : Gas Masks
Subpart L : Chemical-Cartridge Respirators

(12) Title 42, CFR Part 84, Respiratory Protective Devices (June 8, 1995),
Subpart I : Gas Masks
Subpart L : Chemical-Cartridge Respirators

(13) E.S.Moyer, J.A.Peterson and C.Calvert, NIOSH File Report,
  (a) Evaluation of Carbon Tetrachloride Replacement Agents for Testing Organic Vapor Cartridges (1993)
  Later published : Applied Occup. Environ. Hygiene Vol.10, 761-768 (1995)
  (b) Evaluation of Carbon Tetrachloride Replacement Agents for Use in Testing Non-Powered Organic Vapor Chin-Style Canisters (1993)
  Later published : Applied Occup. Environ. Hygiene Vol.10, 769-775 (1995)

(c) Evaluation of Carbon Tetrachloride Replacement Agents for Use in Testing Non-Powered Organic Vapor Front-Mounted/Back-Mounted Canisters (1994)
Center for Disease Control, NIOSH, Division of Safety Research, Certification and Quality Assurance Branch, Air Purifying Respirator Section

(14) R.W.Metzler, Letter to All respirator Manufacturers ;
(a) Subject : Carbon tetrachloride Substitute Test Agent for Nonpowered Negative-Pressure Organic Vapor Cartridges (September 1993)
(b) Subject : Carbon tetrachloride Substitute Test Agent for Nonpowered Negative-Pressure Organic Vapor Chin-Style Canisters (December 1993)
(c) Subject : Carbon tetrachloride Substitute Test Agent for Nonpowered Negative-Pressure Organic Vapor Front-Mounted/Back-Mounted Canisters (March 1994)
(d) Subject : Carbon tetrachloride Substitute Test Agent for Powered Air Purifying Respirators (PAPR) Organic Vapor Cartridges (July 1994)
Department of Health and Human Services, Public Health Service, Centers for Disease Control, NIOSH

(15) S.J.Smith, Comments on Conclusions from Evaluation of Carbon Tetrachloride Replacement Agents for Testing Organic Vapor Cartridges (1993)

(16) CEN 141, Respiratory protection devices - Gas filters and combined filters - Requirements, testing, marking (August 1990)

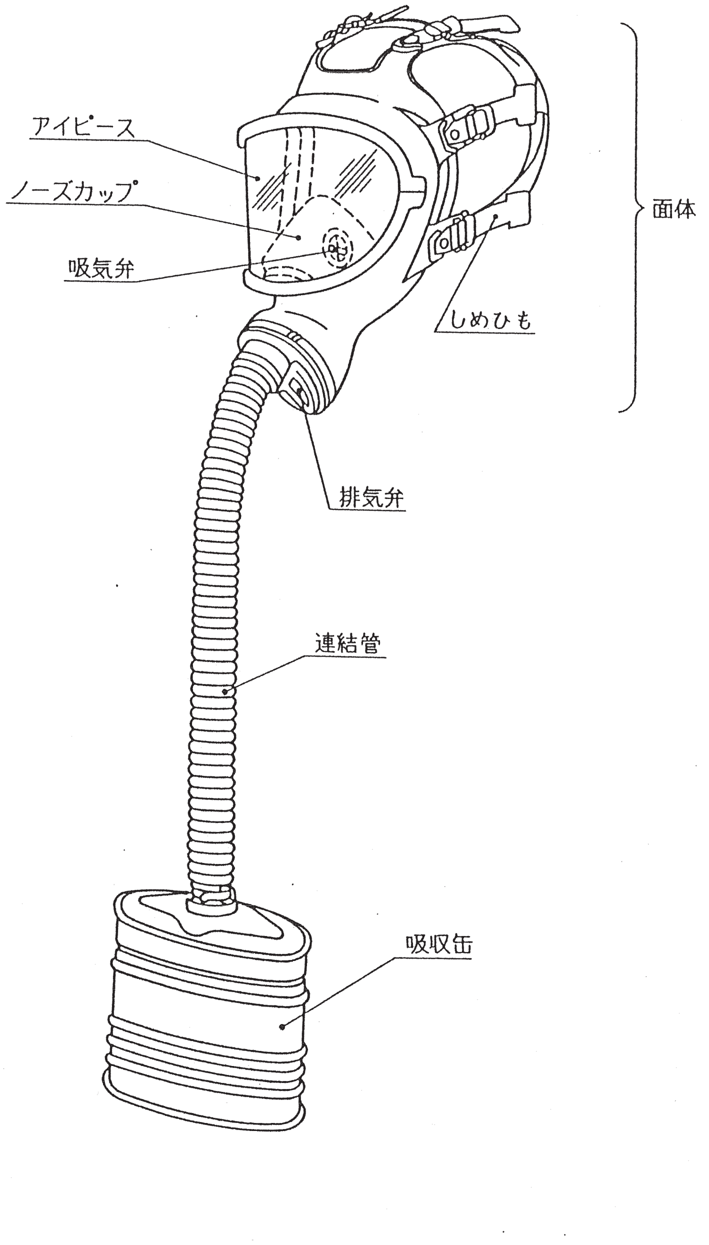
(17) P.Malloy, Technical Advances in Personal Protection, Alternatives to Carbon Tetrachloride for Camister Testing (1994)、 他

(18) Australia, Personal communication (1995)

上記の参考資料の中から(8)、(9)、(10)、(13)、(14)、(15)、(17)、(18)の全文または一部のコピーを本報告書に添付する。その他の本、論文、報告書、規格などは原著を参照されたい。

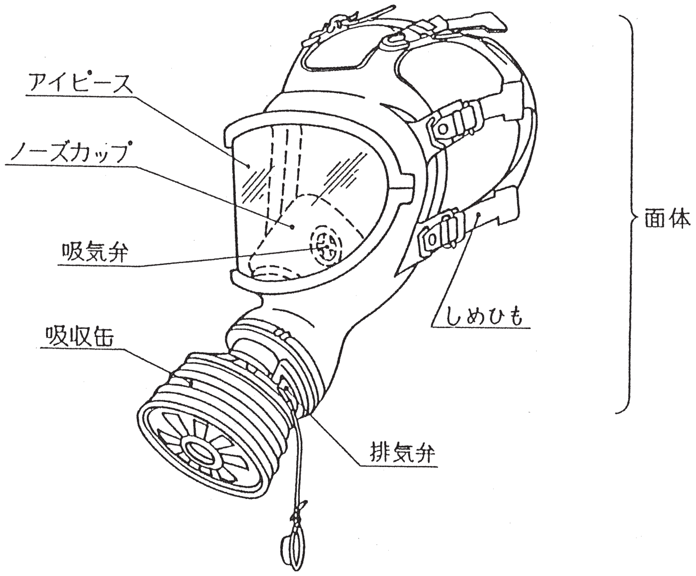
防毒マスクの構造を参考として，次に示す。

（1） 隔離式全面形防毒マスク

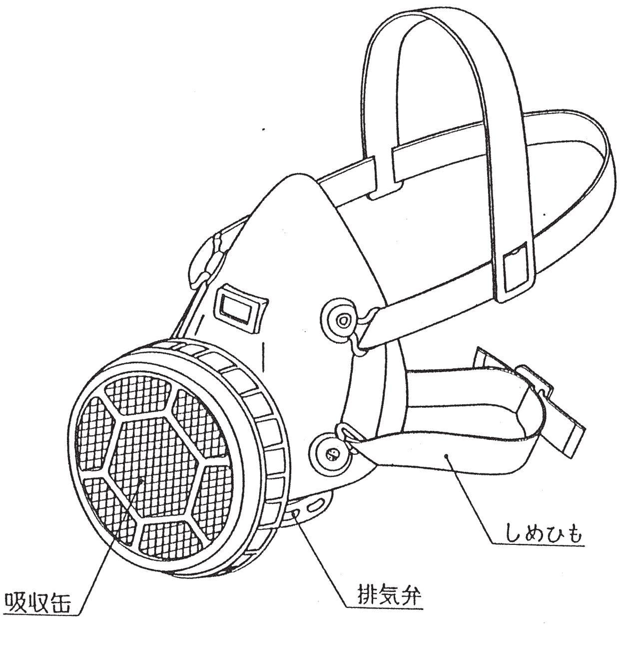


防毒マスク隔離式吸収缶の例（JIS T 8152）

（2） 直結式全面形防毒マスク



（3） 直結式小型半面形防毒マスク



防毒マスク直結式及び直結式小型吸収缶の例
(JIS T 8152)

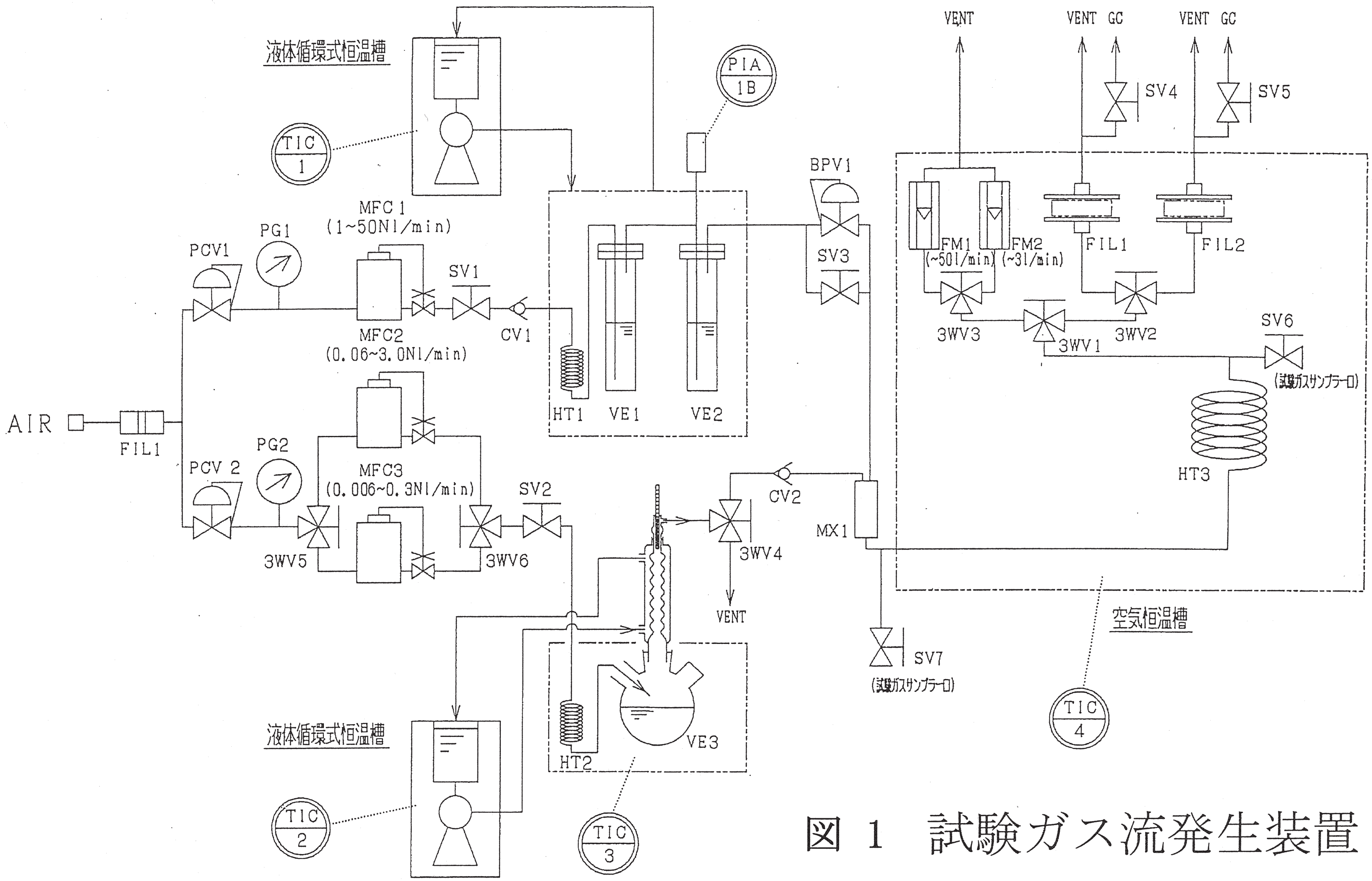


図 1　試験ガス流発生装置

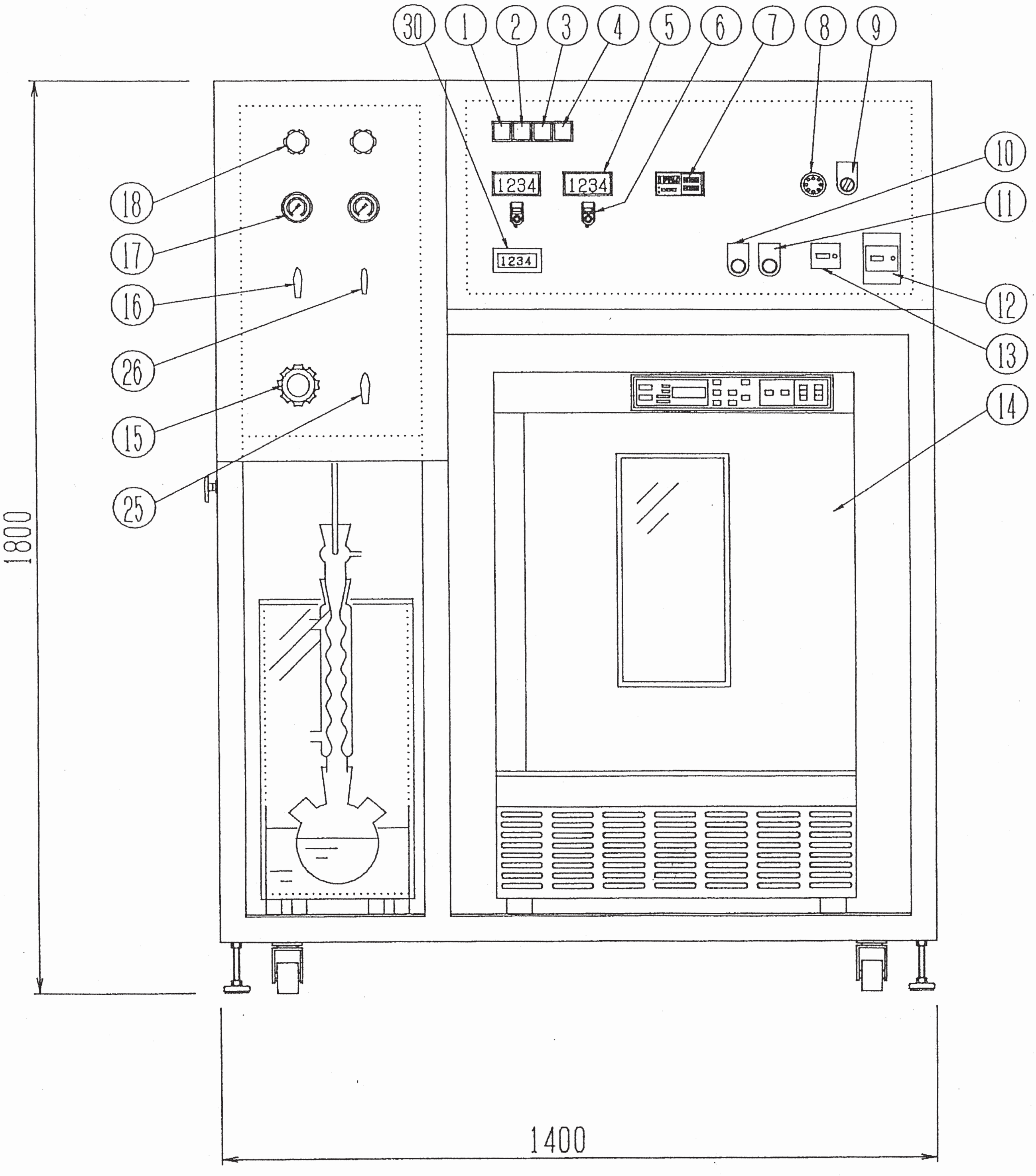


図1-2　試験ガス流発生装置 外観

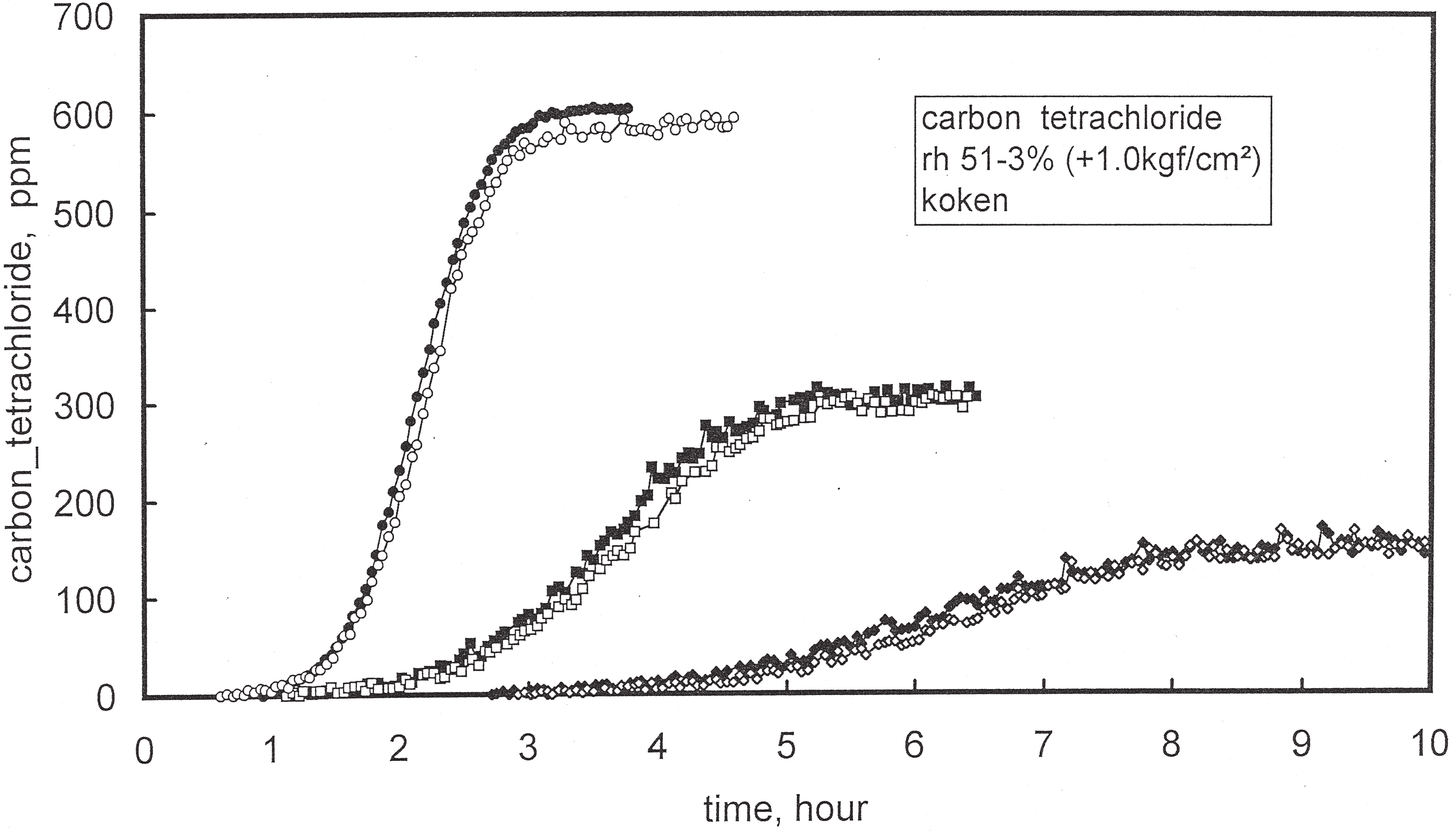


図2　直結式小型Bの吸収缶からの四塩化炭素破過曲線（再現性実験）

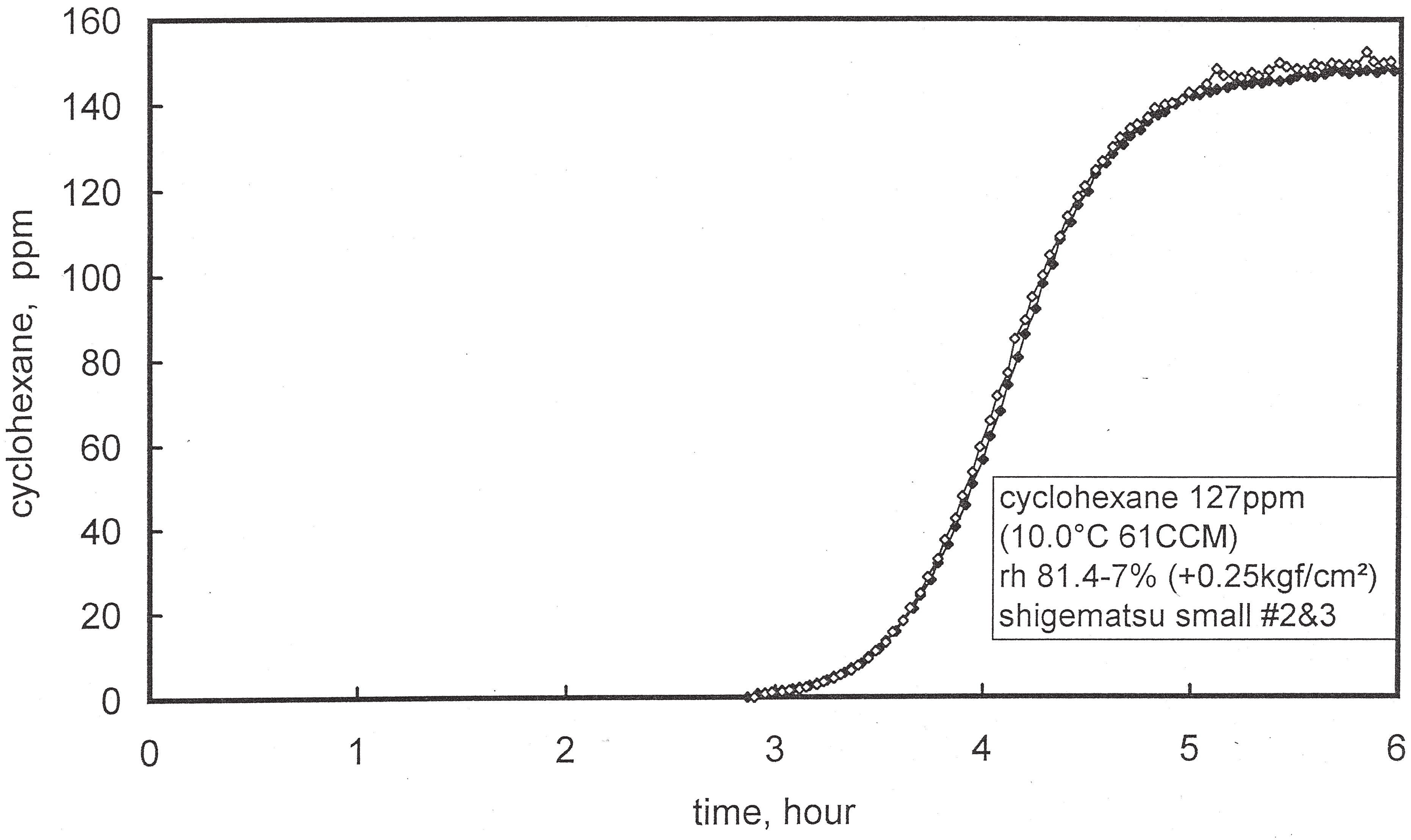


図3 直結式小型Bの吸収缶からのシクロヘキサン破過曲線 (再現性実験)
(シクロヘキサン濃度: 127ppm)

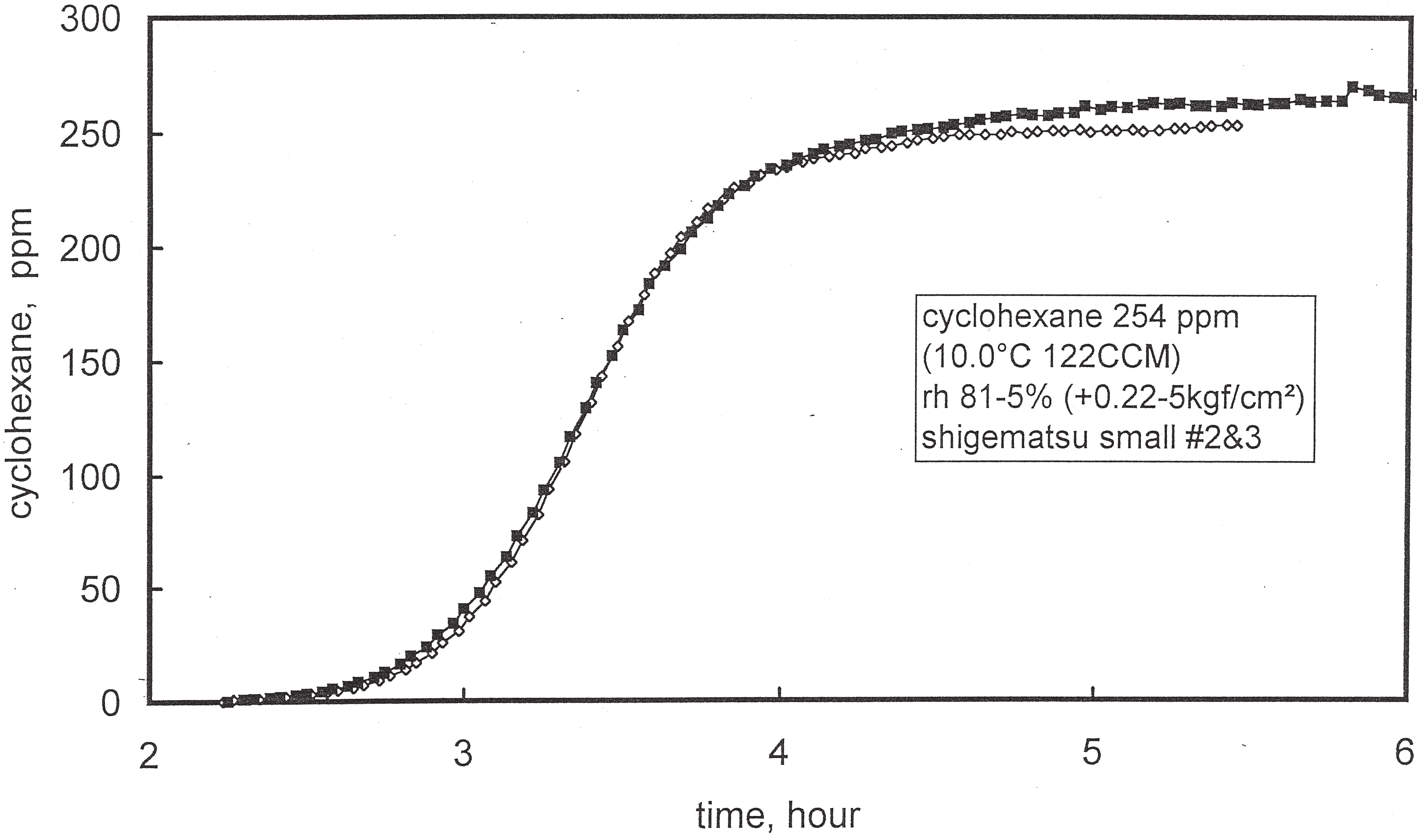


図4　直結式小型Bの吸収缶からのシクロヘキサン破過曲線 (再現性実験)
(シクロヘキサン濃度: 254ppm)

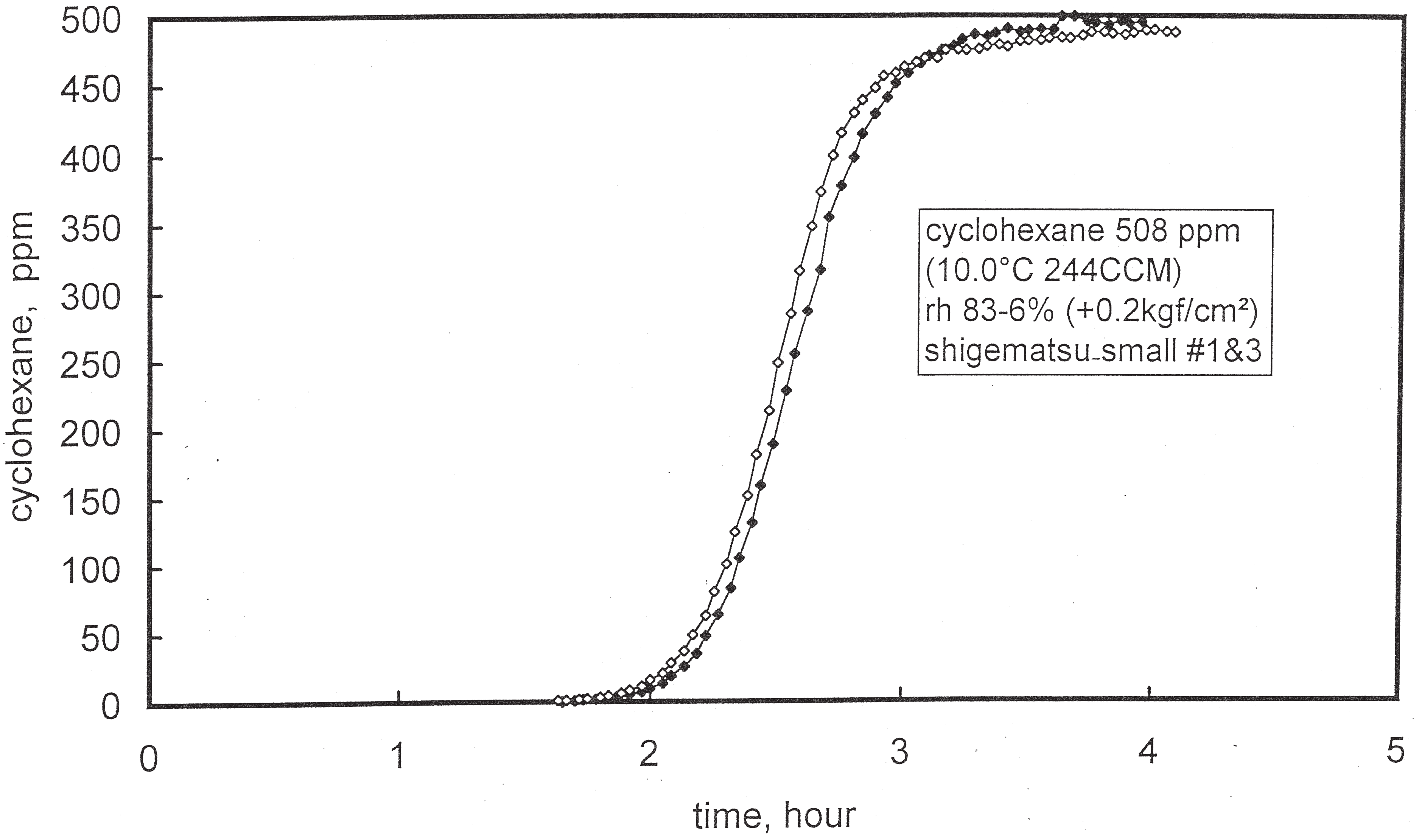


図5 直結式小型Bの吸収缶からのシクロヘキサン破過曲線 (再現性実験)
(シクロヘキサン濃度: 508ppm)

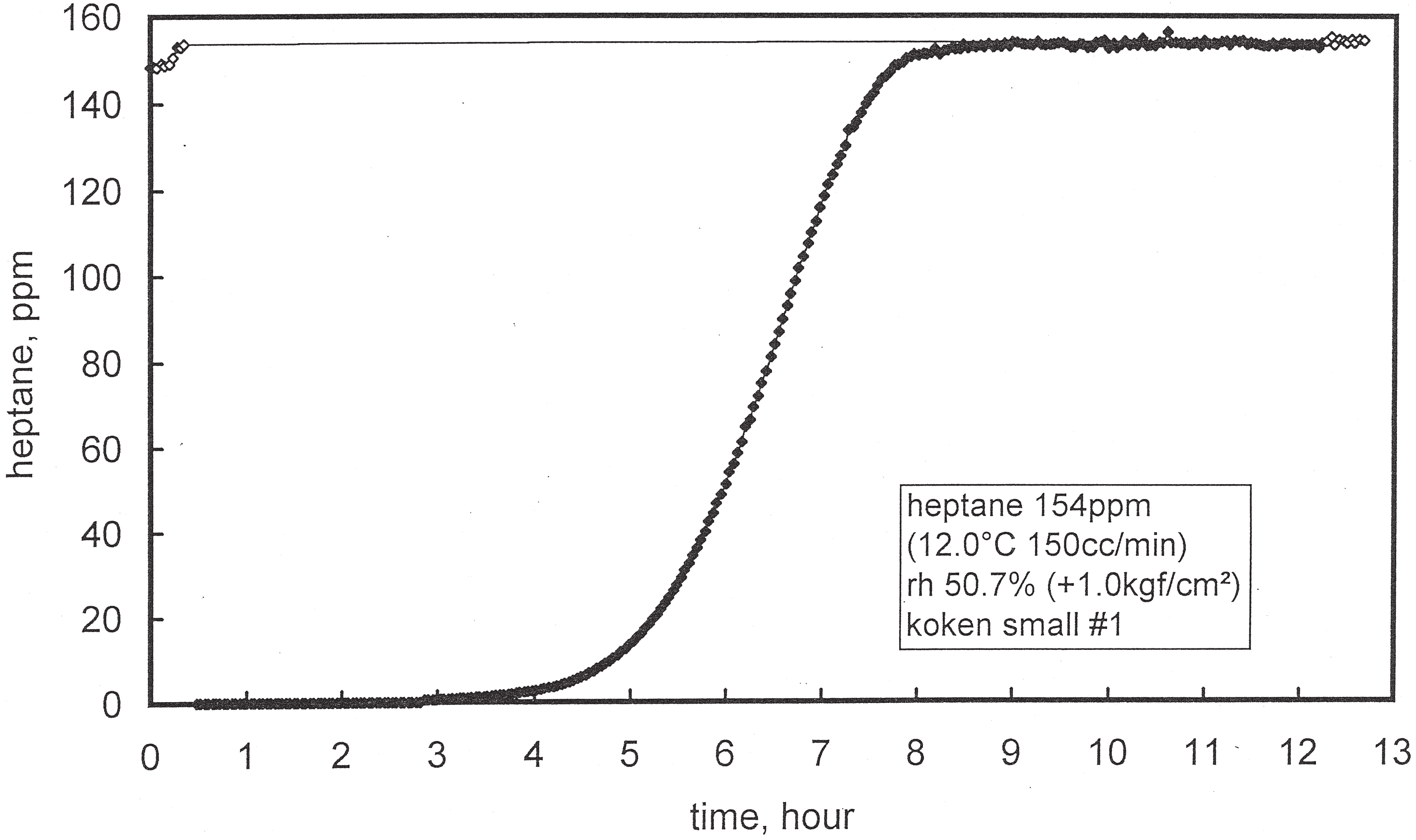


図6 直結式小型Bの吸収缶からのヘプタン破過曲線(ヘプタン濃度154ppm)

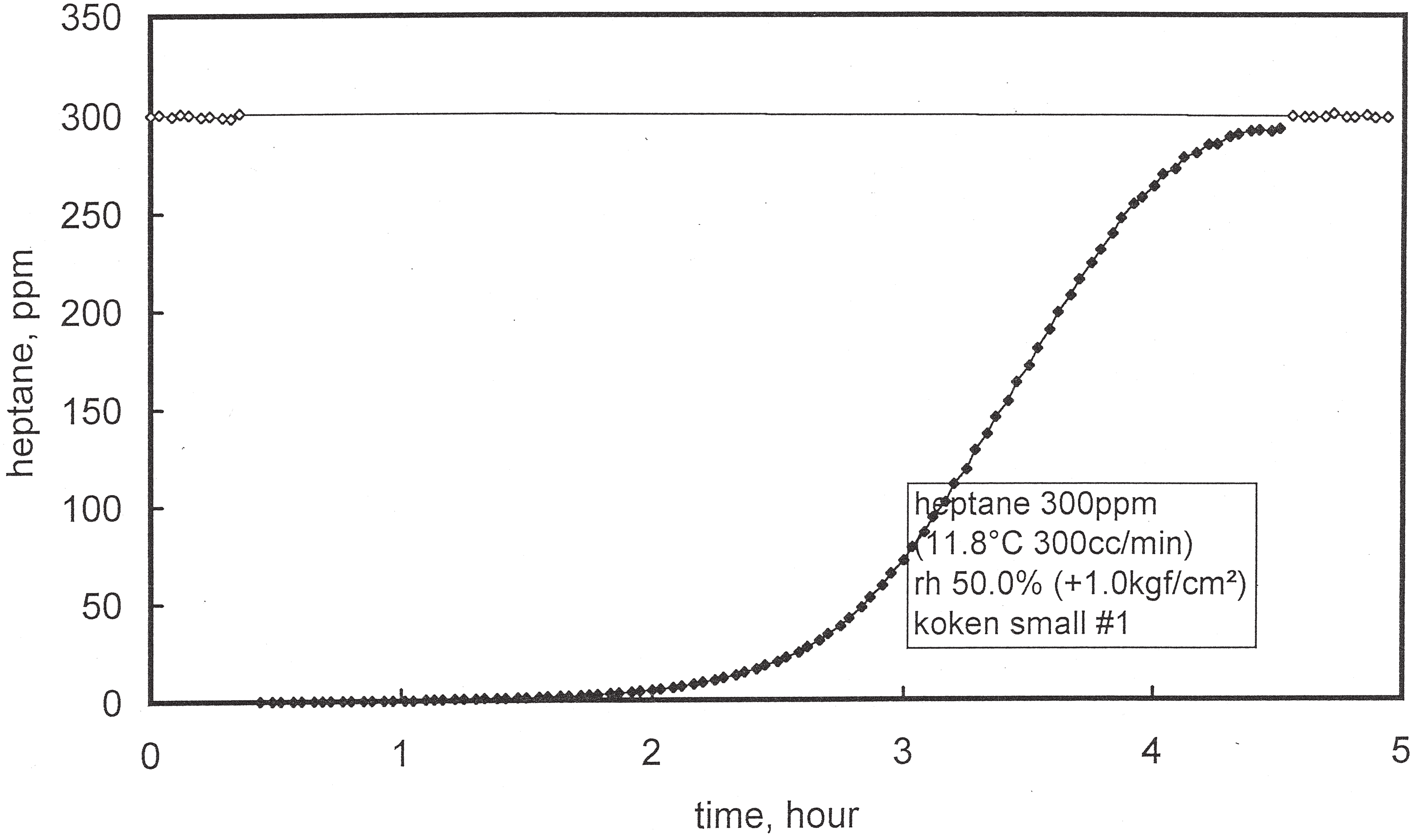


図7 直結式小型Bの吸収缶からのヘプタン破過曲線(ヘプタン濃度300ppm)

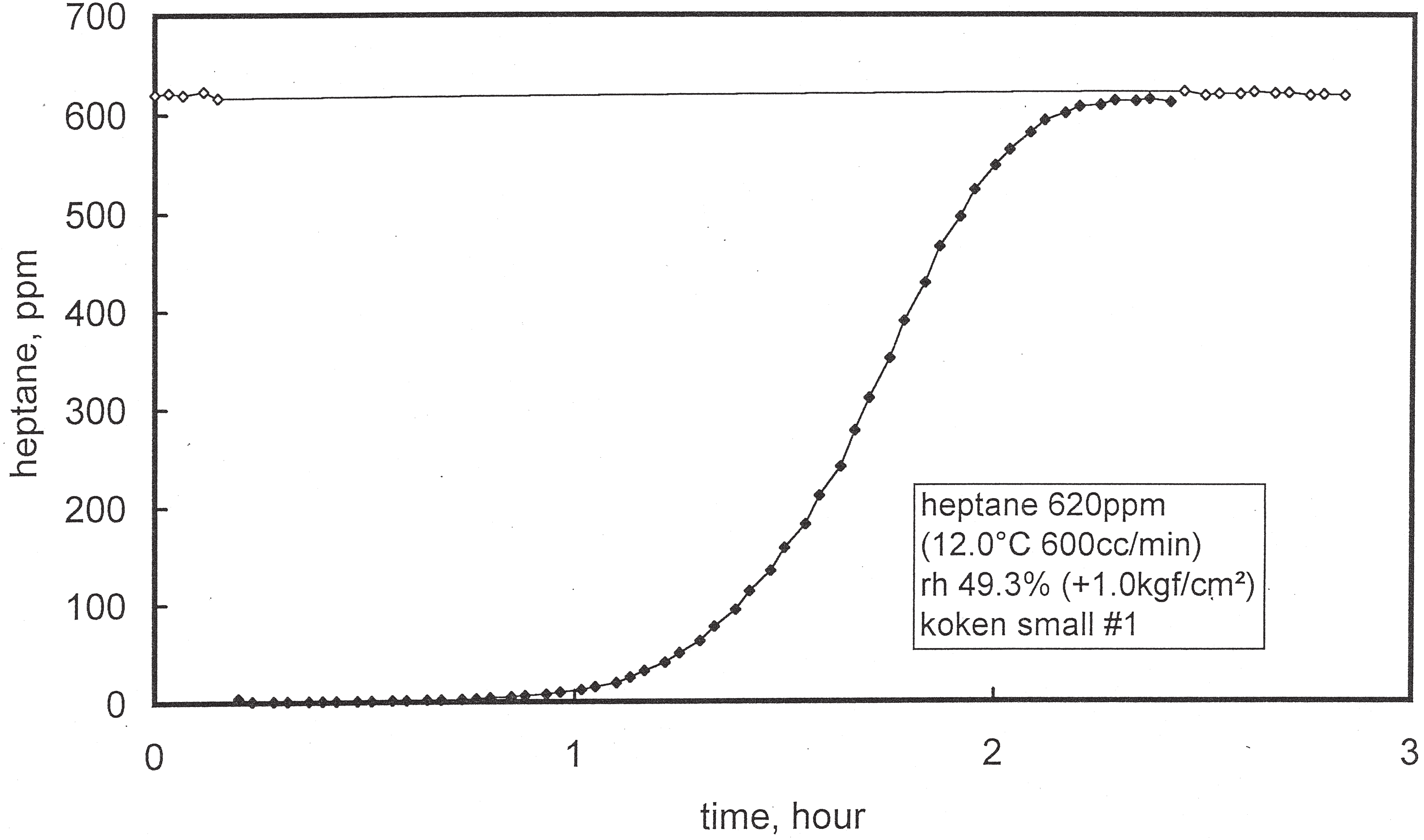


図8　直結式小型Bの吸収缶からのヘプタン破過曲線(ヘプタン濃度620ppm)

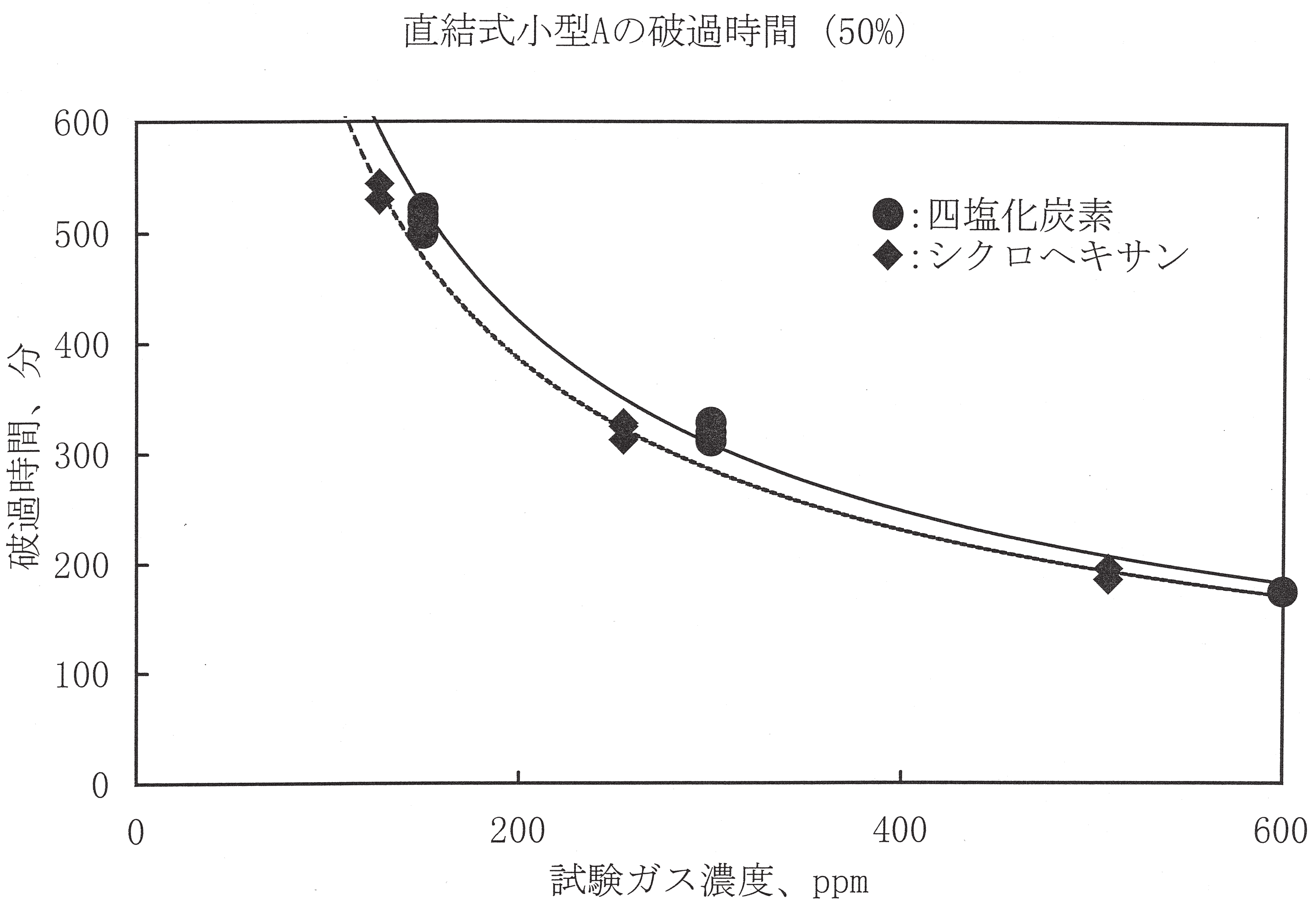


図9　直結式小型Aの吸収缶の破過曲線図(相対湿度50%)

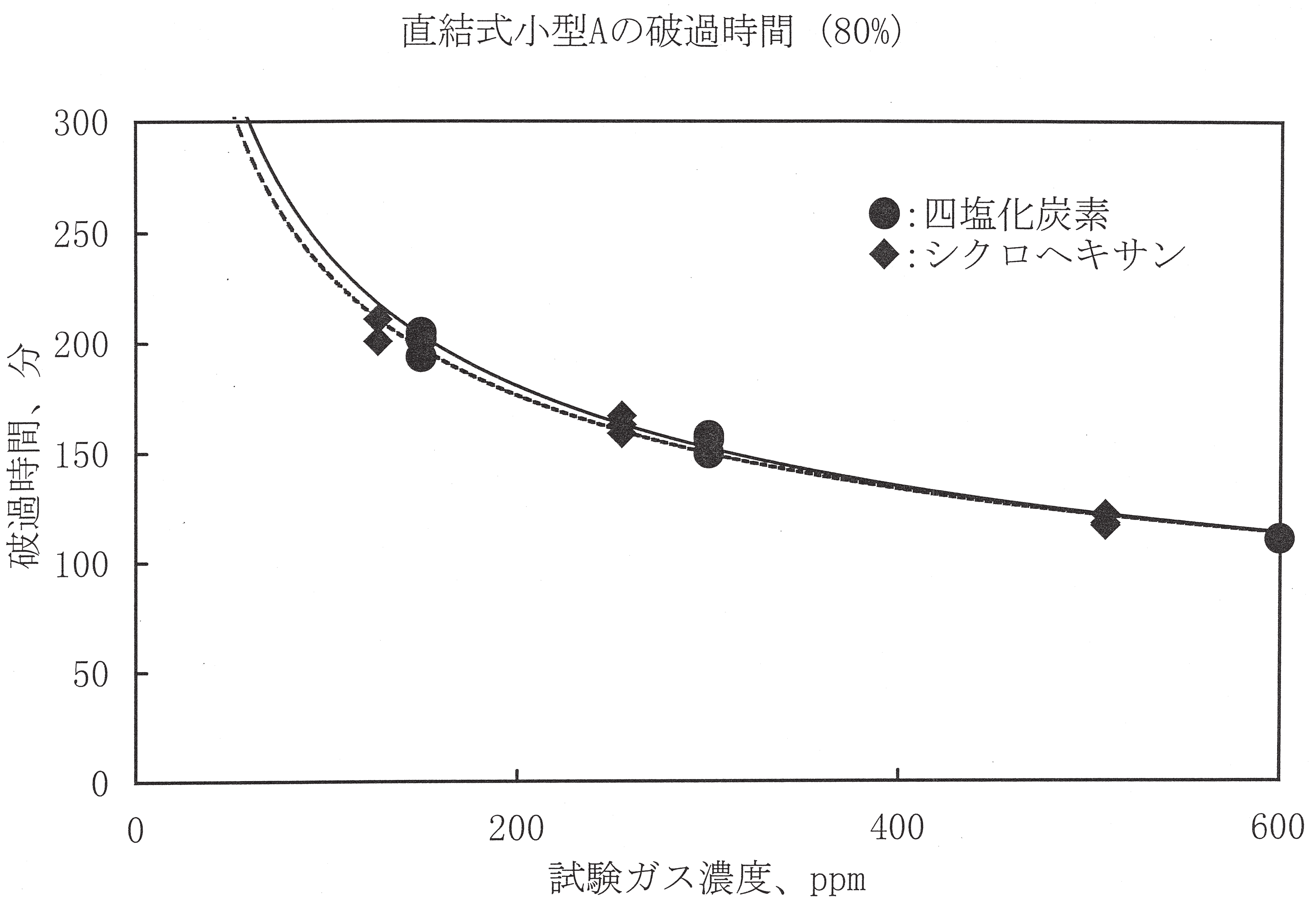


図10　直結式小型Aの吸収缶の破過曲線図(相対湿度80%)

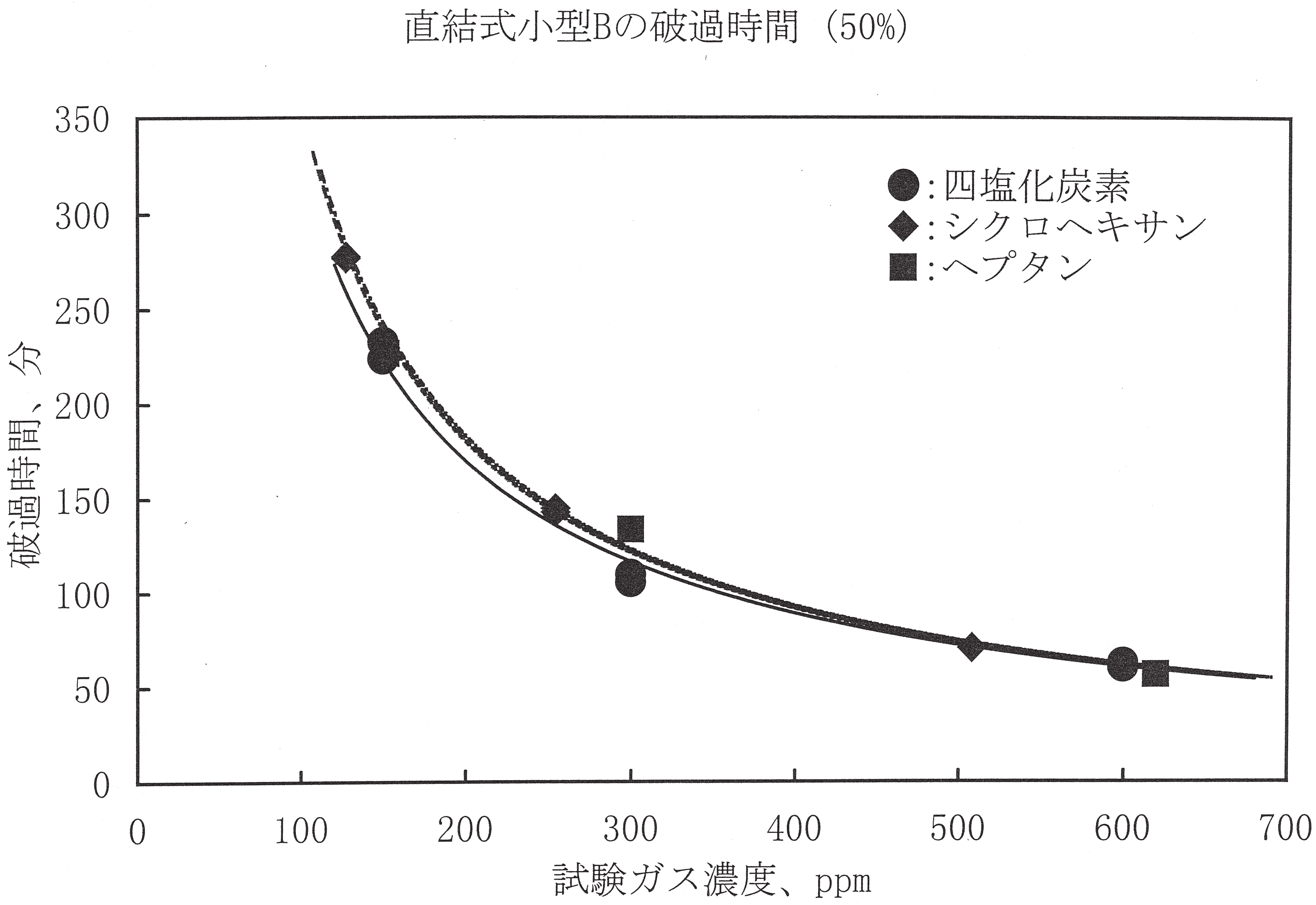


図11　直結式小型Bの吸収缶の破過曲線図(相対湿度50%)

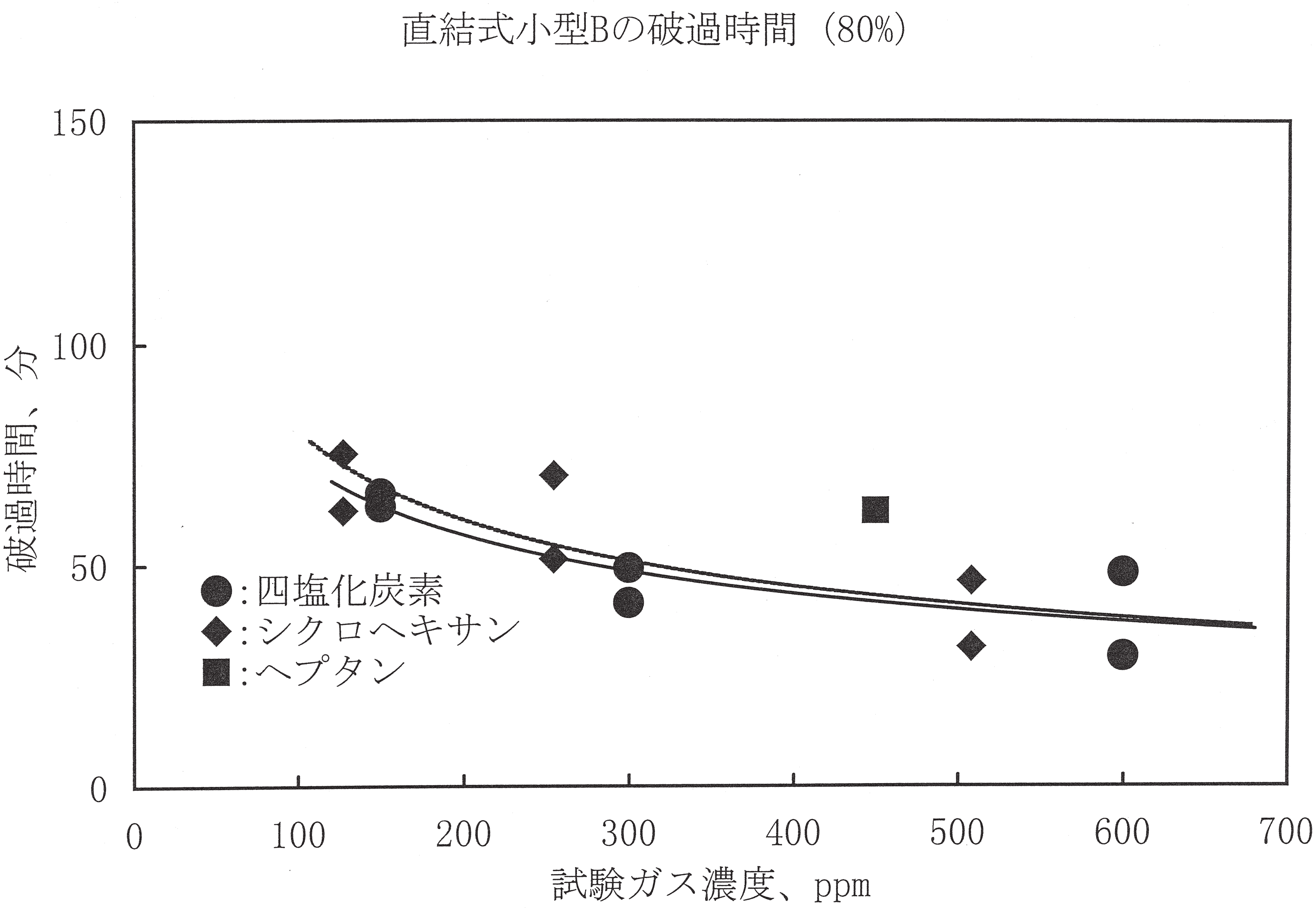


図12　直結式小型Bの吸収缶の破過曲線図(相対湿度80%)

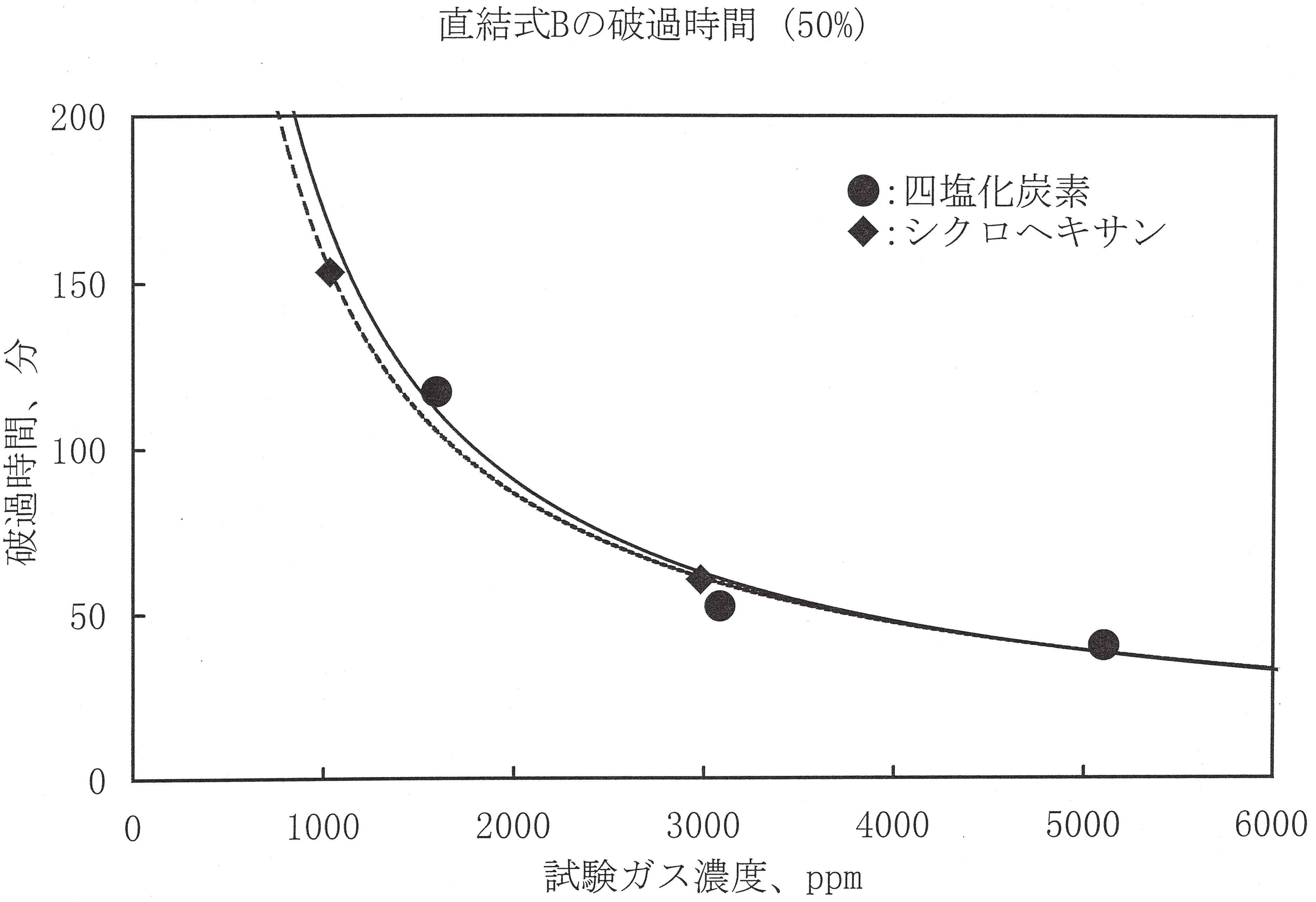


図13　直結式Bの吸収缶の破過曲線図(相対湿度50%)

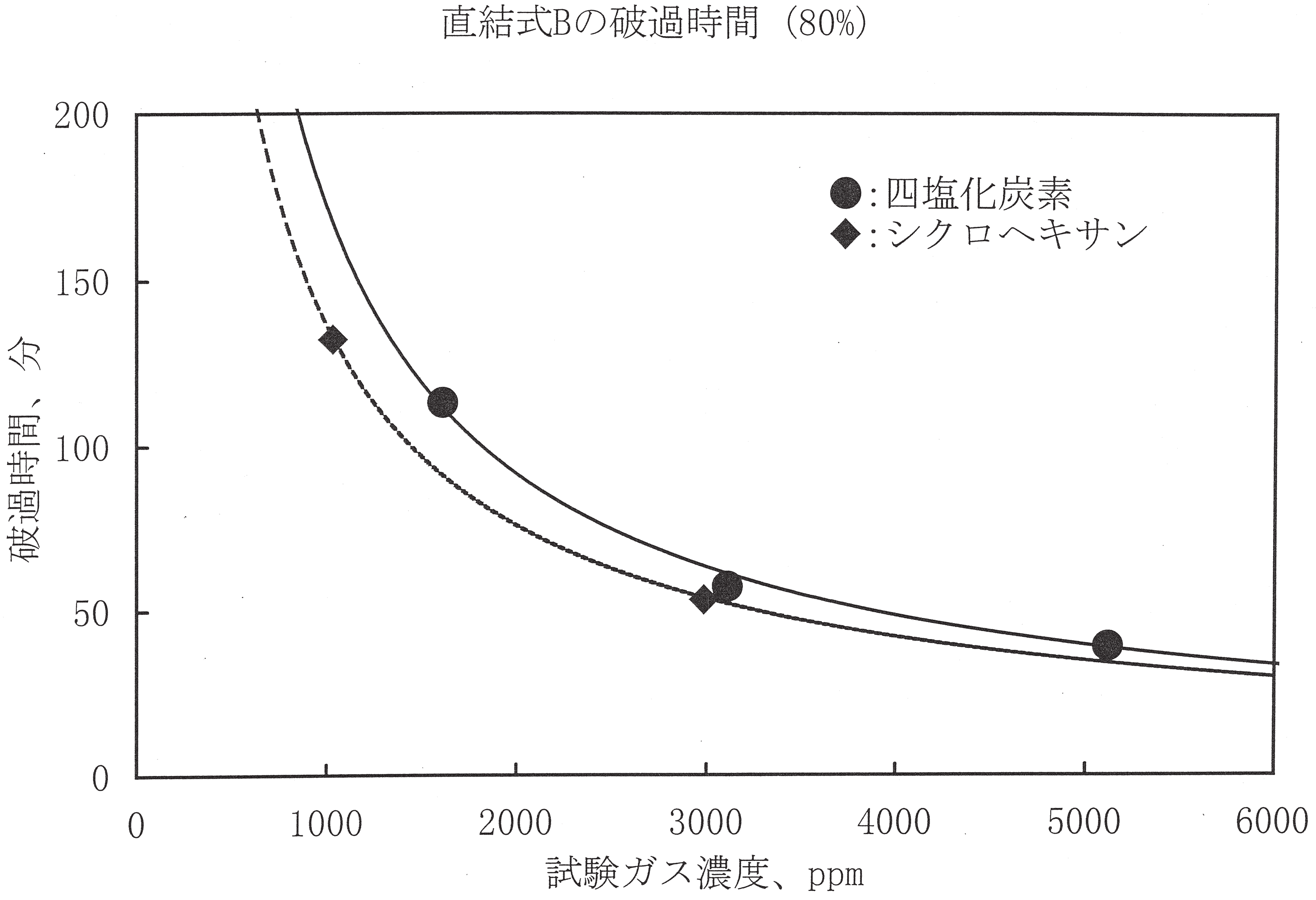


図14　直結式Bの吸収缶の破過曲線図(相対湿度80%)

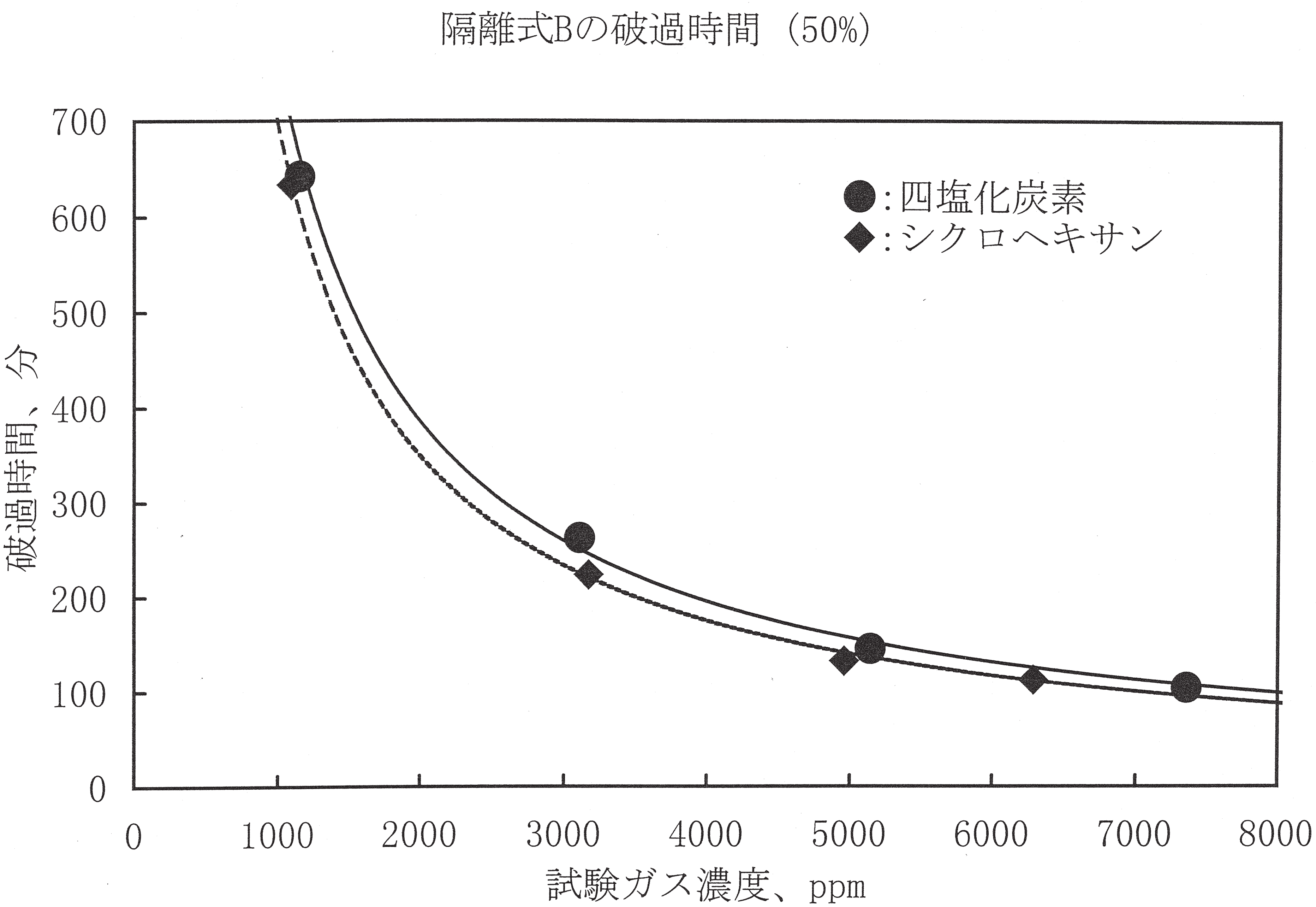


図15　隔離式Bの吸収缶の破過曲線図(相対湿度50%)

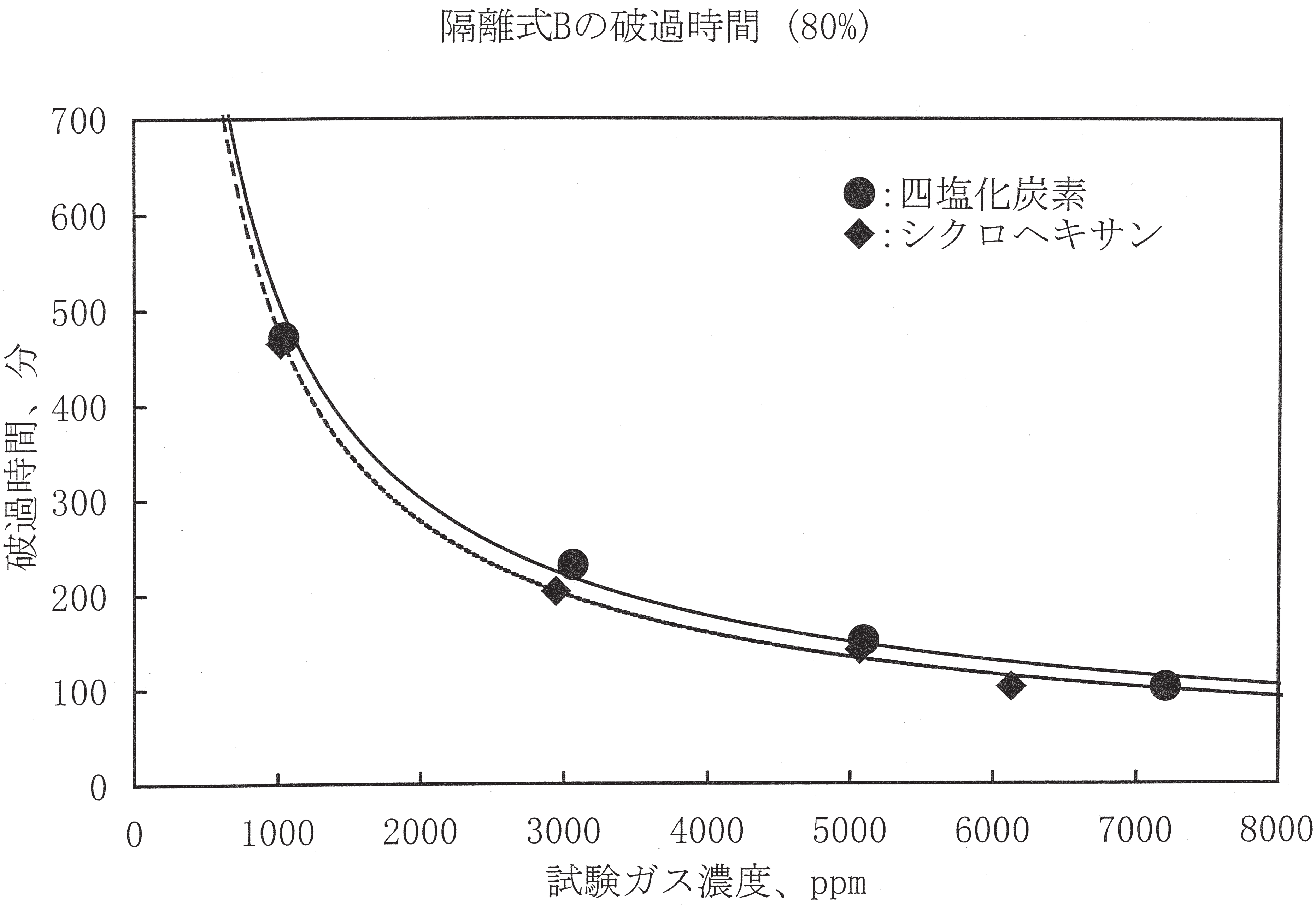


図16　隔離式Bの吸収缶の破過曲線図(相対湿度80%)

資料 8

防毒マスク吸収缶の除毒特性

産業医学総合研究所　松　村　芳　美

1. はじめに

作業環境を汚染する有害ガスから作業者を守る手段として，有害ガスの発生の停止と，環境を浄化するための工学的施設の改善が労働衛生の基本であるが，緊急時や特殊な作業形態のため工学的対策が困難な場合には，防毒マスク，ホースマスク，自給式呼吸具などの個人保護具が使用される。これらの保護具の使用に当っては，夫々の特性に応じて安全に使用するための種々の配慮が必要となる。

防毒マスクの使用は労働安全衛生規則1)，有機溶剤中毒予防規則1)，特定化学物質等障害予防規則1)その他の規則1)によってその着用または作業場における配備が指示されている作業場では勿論のこと，その他の作業場でも有害ガスにばく露される危険のある場合に使用されるが，有害ガス濃度が2％以上（アンモニアについては3％以上）の高濃度の環境や酸欠状態では沪過式呼吸具を使用することはできない。

作業場で防毒マスクを必要とする場合，どの様な基準でマスクの面体や吸収缶を選び，どの様な配慮で使用すべきかということは切実な問題である。しかし，作業形態と有害物の発生状況が異なる個々の作業場に対応出来るような豊富な情報が防毒マスクについて直ちに得られる訳ではない。特に現在，市販されている防毒マスク製品の性能について公表されている報告例は少い。本文は防毒マスクの除毒能力についての情報を集めてその除毒の機構について理解を深め，マスクの適切な選択と使用に役立てることを目的とした。

2. 防毒マスクの種類

防毒マスクは面体と吸収缶から構成されているが，その両方に種々の形と種類がある。我が国で市販されている防毒マスクは JIS T 81522) によって分類されており，隔離式，直結式，直結式小形の三形に大別される。面体は顔面全体を覆う全面形と，顔面の約半分（鼻，口，あご)を覆う半面形がある。面体の選択は，作業に応じた視野の確保，顔面と眼の保護などの必要によって行なわれる。吸収缶には大きさの異なる三形（隔離式，直結式，直結式小形）があり，夫々の形には充塡されている除毒剤の種類の異なる 10 種類から7種類の分類がある。隔離式吸収缶は最も大形で，その重量は 600g から 1kg 位であり，吸収缶はベルトで腰に固定し，ホースで面体と接続して使用する。この吸収缶は高濃度の有害ガスを含む大気（有害ガス含有濃度2％以下，アンモニアは3％以下）中で使用され，耐用時間は吸収缶の種類によって異なるが 40 分から約3時間と比較的長い。各種の隔離式吸収缶の除毒能力についての JIS 規格を表に示した。ただし，表Ⅰの記載の中で充塡されている除毒剤の種類と対象ガスの例として挙げた物質は JIS 規格の範囲ではない。直結式吸収缶は有害ガス含有濃度1％以下（アンモニアは1.5％以下）の中程度のガス濃度の環境を主な対象としており，吸収缶重量は 300g 前後であり，面体に直結して用いる。その耐用時間は吸収缶の種類によって異なるが，JIS に示された条件で測定した場合，10 分から約 80 分までと短時間である。例えばハロゲンガス用吸収缶では，0.3％ の塩素を含む試験気流を毎分 30l の速度で吸引した時に，吸収缶の破過時間が 15 分以上であることが規定されている。直結式小形吸収缶は重量約 100g 前後の小形，軽量のもので，有害ガス濃度 0.1％ 以下の低濃度ガスを含む環境を対象としており，その破過時間は吸収缶の種類により異なるが，標準試験ガス含有空気流に対して 30 分から約 80 分までと比較的長い。例えばハロゲンゲス用直結式小形吸収缶の破過時間は，0.02％ の塩素を含む 30l/分の試験気流に対して 40 分以上であることを JIS は要求している。直結式と直結式小形の種々の吸収缶には，対象ガスを異にする8種類および7種類の分類がある。しかし，一酸化炭素用と消防用の吸収缶は直結式には含まれておらず，直結式小

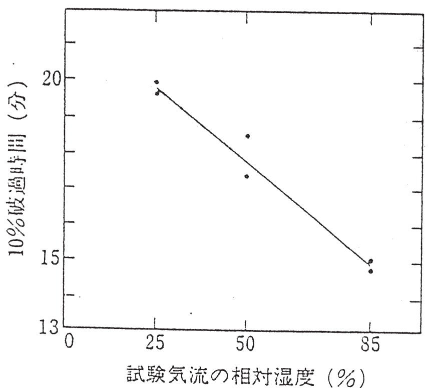


図 14　活性炭を充塡したカートリッジの塩化ビニル（600 ppm）に対する破過時間と試験気流中の相対湿度の関係（Smith らの報告による[18]）
試験気流の温度は 24°C，流速は 30 l/分である

50 および 85%，流速 30 l/分である。キャニスターの破過時間測定条件は蒸気濃度 100—5,000 ppm，温度 24°C，相対湿度 50%，流速 60 l/分である。この様な条件での吸収缶破過時間の測定値の一部を図 13 と図 14 に示した。これらの測定では，流出ガス濃度が流入ガス濃度の 10% に達した時間を破過時間としている。塩化ビニルに対する活性炭カートリッジの破過時間については Miller と Reist[19] の報告も見られる。

活性炭を充塡したカートリッジ形の吸収缶の有機化合物蒸気に対する除毒特性について広範囲の研究が Nelson と共同研究者達によって行われた[20)~25)]。彼等の研究項目は，吸収缶の破過時間測定のための試験気流として定常流と脈動流の比較，種々の有機化合物蒸気に対する破過時間の測定，有機化合物蒸気濃度や相対湿度などの試験ガスの条件の変化に対応する破過時間の変化の関係，等である。彼らの膨大な種類の有機化合物蒸気に対する活性炭吸収缶の破過時間の測定値から，系列的な有

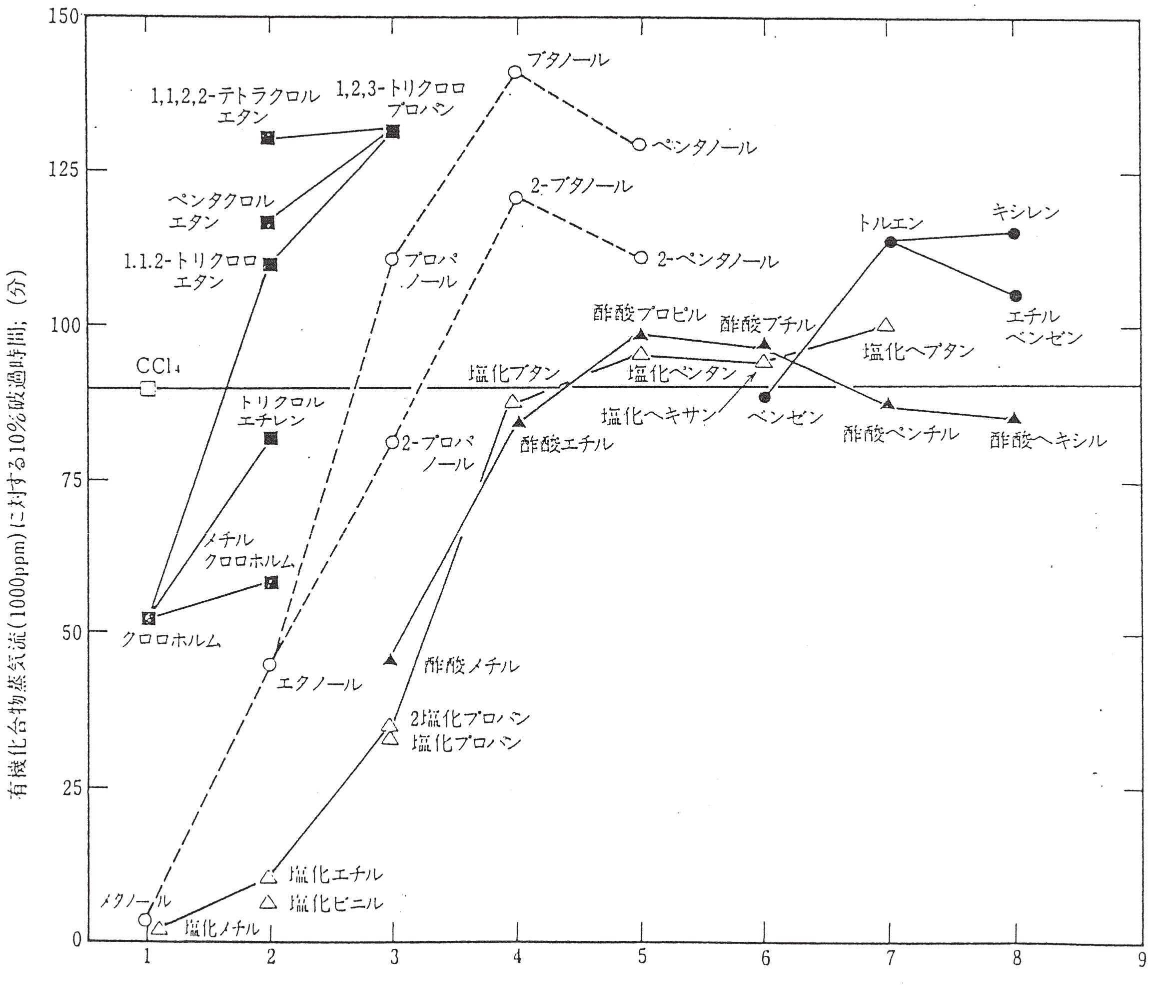


図 15　活性炭吸収缶の種々の有機化合物蒸気に対する破過時間（Nelson 等の報告による[22]）

資料 9

Respirator Cartridge Efficiency Studies:
V. Effect of Solvent Vapor

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We have determined the service lives of organic vapor respirator cartridges for 121 solvent vapors and gases including aromatics, alcohols, acetates, alkanes, ketones, amines, and chlorinated materials. We passed the vapor and air mixtures through the cartridges and monitored the downstream concentration with a flame ionization detector (FID). Monitoring continues until the cartridge is completely saturated. We compared breakthrough times to values calculated from the adsorption isotherm and Mecklenburg equation and obtained reasonable agreement. In general. the activated carbon has greater affinity for the less volatile materials. Also, the higher the boiling point of the solvent, the greater is the weight of solvent adsorbed. Water vapor, in general, decreases the amount of solvent vapor adsorbed, especially of the more volatile solvents and those soluble in water. The effect of concentration on breakthrough time was briefly investigated and found to conform to the basic Freundlich equation.

Introduction

THIS IS THE FIFTH in a series of papers concerning respirator cartridge efficiency. The previous reports have described our program goals,[1] the testing apparatus,[2] development of a mechanical breathing simulator,[3] and a comparison of the effects of steady-state and pulsating flow.[4]

We observed no significant difference in cartridge service life between steady-state and pulsating flow. This conforms to basic adsorption theory; equilibrium between the vapor and adsorbent should be practically instantaneous.[5] We discarded the breathing simulator, therefore, and in all subsequent testing employed steady-state flow.

We also observed that the amount of solvent adsorbed at a given temperature, humidity, and concentration is essentially constant (see Figure 1) and is independent of the flow rate in the range normally associated with human breathing. Since the equilibrium rates are so rapid, the time to reach a predetermined breakthrough is inversely proportional to the flow rate. That is, doubling the flow through the cartridges will halve the effective service life if all the other test parameters remain the same.

The present investigation sought to determine how the cartridge service life varies with the type of solvent vapor adsorbed. We investigated 121 solvent vapors and gases and compared observed breakthrough times with the values calculated from the adsorption isotherm and the Mecklenburg equation. This report, in some respects, respresents an

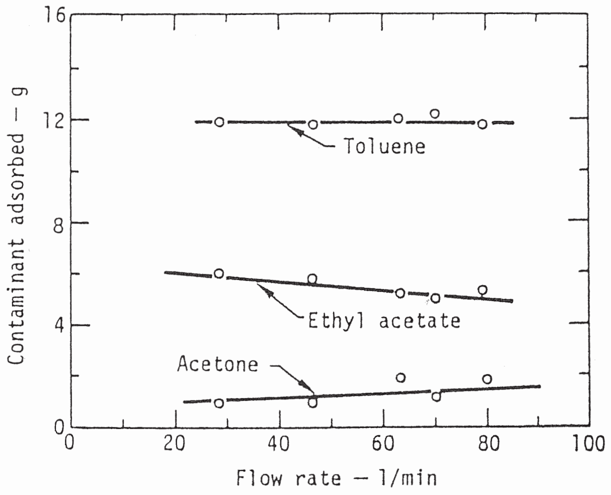

Figure 1. Contaminant adsorbed as a function of flow rate.

This work was performed under the auspices of the United States Atomic Energy Commission.

extension of the investigation by Freedman *et al.*[6]

Our standard test conditions included a solvent concentration of 1000 ppm, 50% relative humidity, and 53.3-liter/min flow, equivalent to a moderately heavy work rate of 830 kg-m/min. The solvents tested included aromatics, alcohols, actetates, alkanes, ketones, amines, and chlorinated materials. Some preliminary investigations on the effect of concentration (125 to 2000 pp) were also initiated.

Experimental Procedure

The apparatus used to generate and monitor the test concentrations is basically the same as that described in refs. 2 and 4. Several minor changes appear in Figure 2.

The humidifier now consists of a Lucite reservoir with a level switch and solenoid valve assembly to maintain a constant water volume. A 126-watt spot heater on the reservoir bottom controlled by a humidity monitor holds the humidity constant.

A 2-inch plug of glass wool added to the solvent vapor injection port aids in evaporating the solvents, especially those with higher boiling points. Maintaining the block temperature as close to the boiling point as possible avoids decomposing the solvent and plugging the needle. The activated carbon plug downstream further smooths solvent evaporation irregularities.

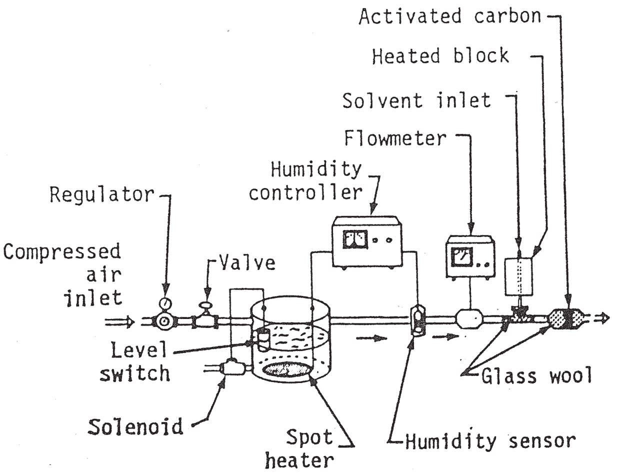

Figure 2. Schematic diagram of humidifier and solvent vaporizer.

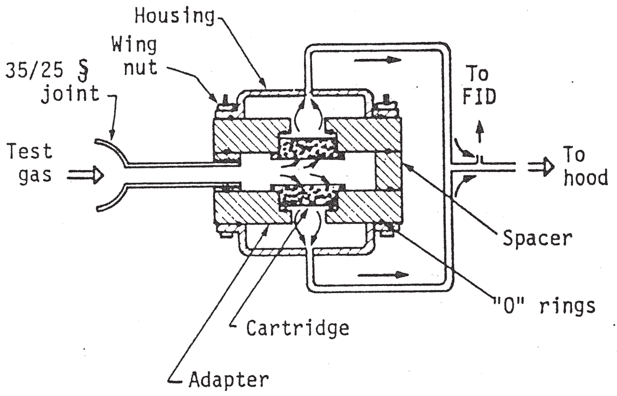

Figure 3. Schematic diagram of dual cartridge holder.

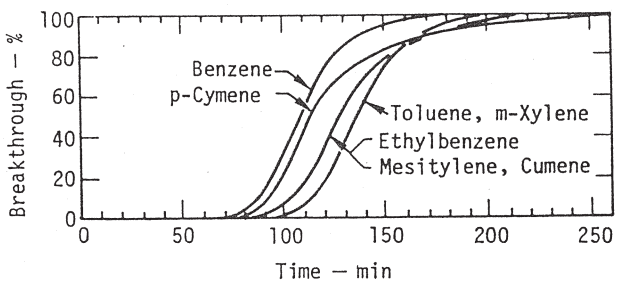

Figure 4. Breakthrough curves for aromatics boiling in the range 80° to 177°C.

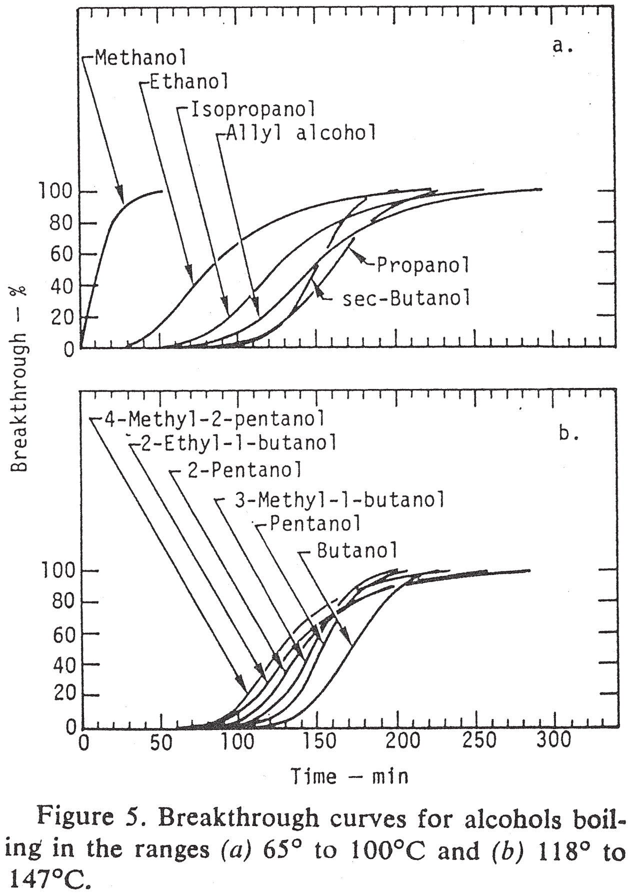

Figure 5. Breakthrough curves for alcohols boiling in the ranges *(a)* 65° to 100°C and *(b)* 118° to 147°C.

The cartridges were vacuum-dried and stored in a cabinet for at least 2 days at 50% relative humidity and 22°C.[4] Two cartridges were tested simultaneously in the parallel configuration shown in Figure 3.

The test gas entered through a 35/25 ground brass socket joint and passed through the cartridges held in individual polyethylene adaptors. Anodized aluminum housings, secured with wing nuts, collected the down-s and conducted them to the common sample outlet.

Type 1 cartridges (see ref. 4 for cartridge

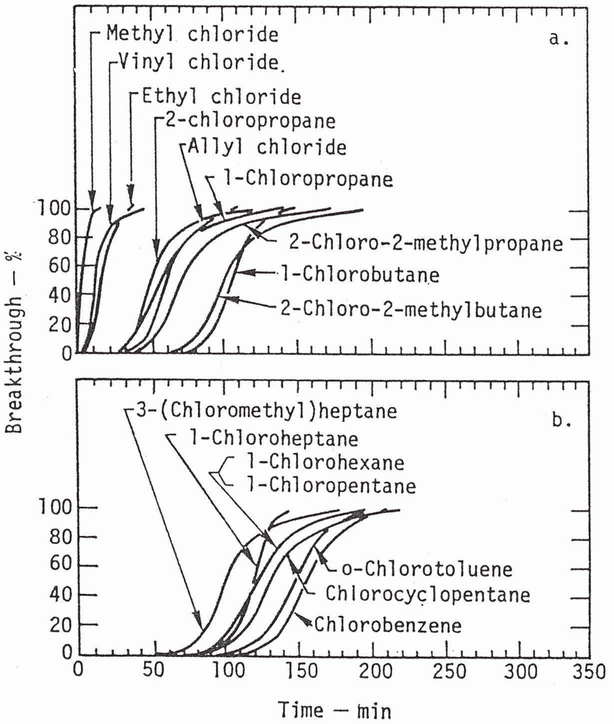

Figure 6. Breakthrough curves for monochlorides boiling in the ranges *(a))* −24° to 86°C and *(b)* 108° to 172°C.

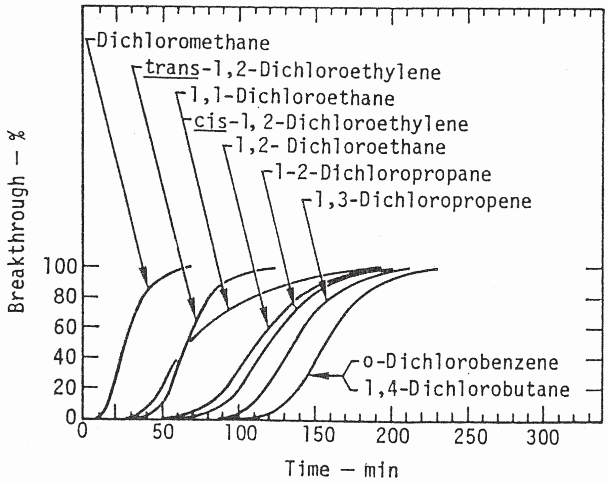

Figure 7. Breakthrough curves for dichlorides boiling in the range 40° to 180°C.

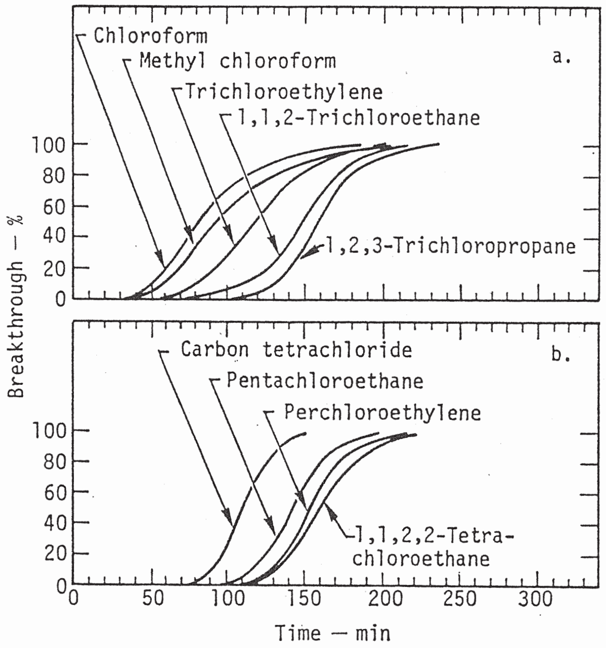

Figure 8. Breakthrough curves for *(a)* trichlorides and *(b)* tetra- and pentachlorides boiling in the ranges 61° to 156°C and 77° to 161°C, respectively.

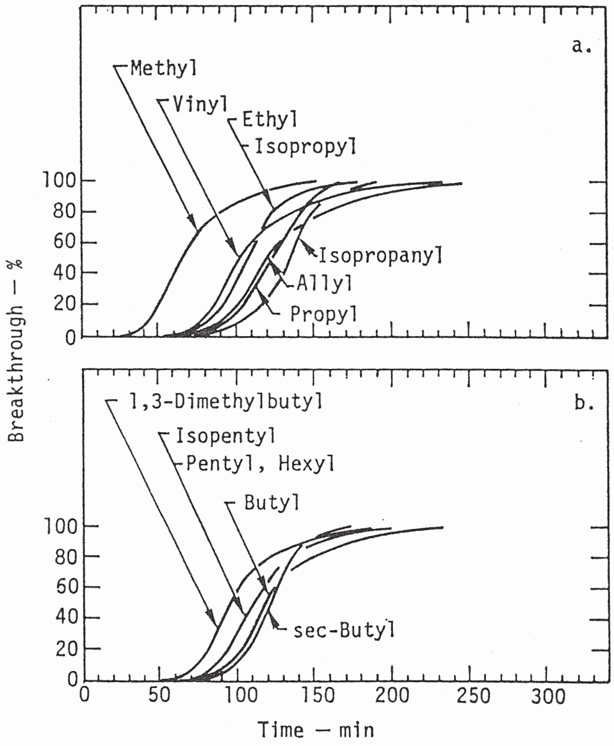

Figure 9. Breakthrough curves for acetates boiling in the ranges *(a)* 57° to 104° and *(b)* 112° to 169°C.

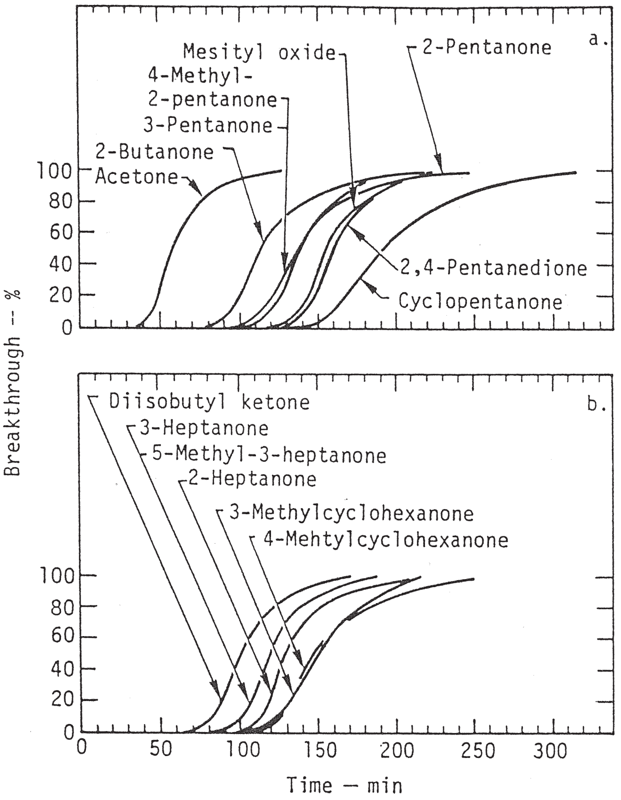

Figure 10. Breakthrough curves for ketones boiling in the ranges *(a)* 56° to 104°C and *(b)* 112° to 169°C.

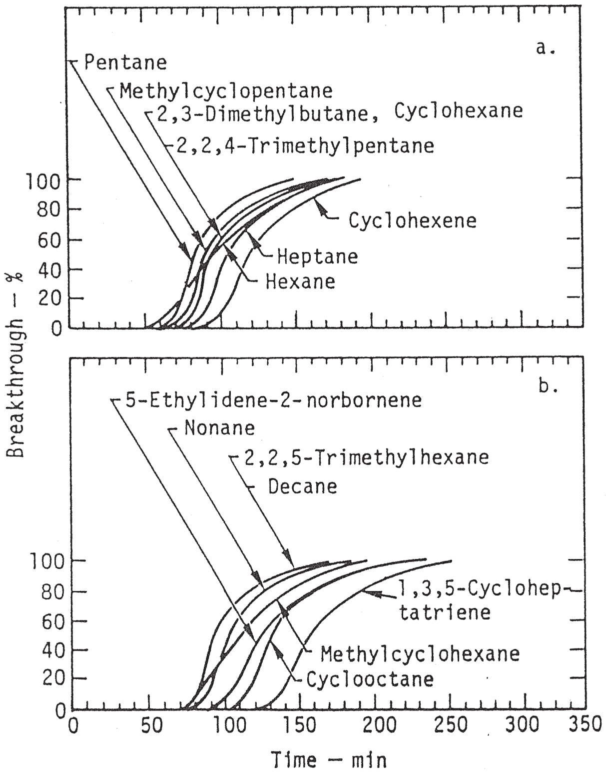

Figure 11. Breakthrough curves for alkanes boiling in the ranges *(a)* 39° to 99°C and *(b)* 101° to 174°C.

characteristics) were tested with aromatics, alcohols, esters, and chlorinated materials; type 2 cartridges were tested with ketones, alkanes, amines, and most miscellaneous compounds.

Results

Effect of Solvent Vapor

Figures 4 through 13 show how the cartridge service life varies when tested with each class of solvent vapor. The percent breakthrough (the ratio of the downstream

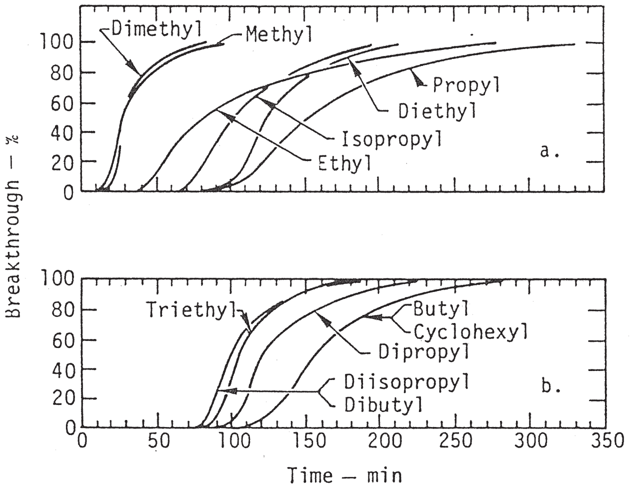

Figure 12. Breakthrough curves for amines boiling in the ranges *(a)* −7° to 56°C and *(b)* 78° to 159°C.

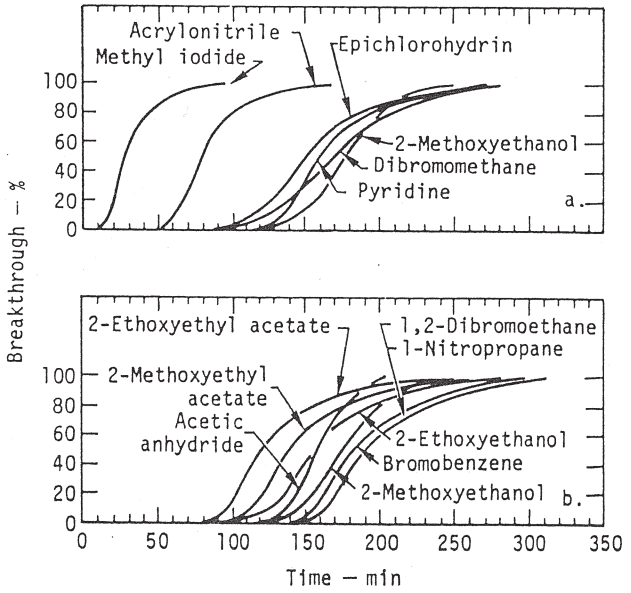

Figure 13. Breakthrough curves for miscellaneous solvents boiling in the ranges *(a)* 42° to 124°C and *(b)* 132° to 156°C.

TABLE I

Solvent	BP (C°)	Vapor pressure at 20°C (Torr)	Diffusion coefficient at 25°C (cm^2/sec)	Volume charcoal (ml)[a]	Weight charcoal (g)[b]	Experimental breakthrough times			Wt. solvent adsorbed per wt. of carbon			Weight water adsorbed at $t_{100\%}$ per wt. carbon[f] (g/g)
						$t_{1\%}$ (min)	$t_{10\%}$ (min)	$t_{99\%}$ (min)	$t_{1\%}$[c] (g/g)	$t_{10\%}$[d] (g/g)	$t_{100\%}$[e] (g/g)	
Aromatics[g]												
Benzene	80.1	72.4	0.0932	146	59.1	73.3	88.6	170	0.214	0.249	0.327	0.035
Toluene	110.6	21.8	0.0849	144	57.5	94.3	114	196	0.334	0.397	0.473	-
Ethyl benzene	136.2	7.08	0.0755	148	55.9	83.7	105	223	0.352	0.432	0.573	0.021
m-Xylene	138.4	6.16	0.0670	148	59.7	98.7	116	193	0.388	0.450	0.536	-
Cumene	152.4	3.34	0.0677	146	60.0	81.2	103	153	0.359	0.447	0.538	0.022
Mesitylene	164.7	1.73	0.0663	147	59.5	85.5	105	189	0.382	0.460	0.565	-
p-Cymene	176.7	1.28	0.0630	148	56.9	75.6	92.9	253	0.394	0.476	0.594	-
Alcohols[g]												
Methanol	64.7	96.8	0.1520	148	55.4	0.2	3.2	47.0	0.0003	0.004	0.018	0.091
Ethanol	78.4	43.6	0.1181	146	55.5	28.0	45.3	207	0.051	0.079	0.168	0.135
Isopropanol	82.3	32.4	0.1013	145	55.7	54.3	81.8	247	0.129	0.188	0.314	0.133
Allyl alcohol	97.0	21.4	0.1021	145	55.4	65.5	105	280	0.152	0.234	0.362	0.117
Propanol	97.1	14.4	0.0993	144	55.7	70.4	111	250	0.168	0.255	0.384	0.065
sec-Butanol	99.5	12.6	0.0891	144	55.9	96.0	121	196	0.281	0.347	0.438	0.050
Butanol	117.7	5.65	0.0861	143	55.5	115	141	235	0.340	0.409	0.512	0.016
2-Pentanol	119.9	4.36	0.0728	147	56.7	86.8	111	277	0.298	0.373	0.517	0.020
3-Methyl-1-butanol	131.2	2.4	0.0709[h]	147	55.0	97.0	121	195	0.344	0.421	0.525	0.047
4-Methyl-2-pentanol	131.8	3.9	0.0653[h]	148	55.7	75.4	96.1	243	0.306	0.382	0.545	0.041
Pentanol	137.9	1.82	0.0716	148	55.0	102	130	208	0.362	0.451	0.552	0.019
2-Ethyl-1-butanol	146.8	1.56	0.0653[h]	150	55.7	76.5	101	257	0.310	0.400	0.582	0.030

TABLE I (Continued)

Solvent	BP (C°)	Vapor pressure at 20°C (Torr)	Diffusion coefficient at 25°C (cm^2/sec)	Volume charcoal (ml)[a]	Weight charcoal (g)[b]	Experimental breakthrough times			Wt. solvent adsorbed per wt. of carbon			Weight water adsorbed at $t_{100\%}$ per wt. carbon[f] (g/g)
						$t_{1\%}$ (min)	$t_{10\%}$ (min)	$t_{99\%}$ (min)	$t_{1\%}$[c] (g/g)	$t_{10\%}$[d] (g/g)	$t_{100\%}$[e] (g/g)	
Monochlorides[g]												
Methyl chloride	-24.2	3460	0.1140[h]	148	55.7	0.05	0.7	14.6	0.0001	0.001	0.008	0.074
Vinyl chloride	-13.9	2310	0.0995[h]	147	55.7	3.8	6.6	46.3	0.009	0.016	0.038	0.070
Ethyl chloride	12.3	1110	0.0950[h]	148	56.1	5.6	10.7	38.7	0.014	0.026	0.048	0.096
2-Chloropropane	35.2	430	0.0819[h]	148	56.8	26.1	35.9	109	0.080	0.107	0.167	0.018
Allyl chloride	44.5	300	0.0975	141	55.5	30.5	44.6	108	0.093	0.132	0.194	0.040
1-Chloropropane	46.7	277	0.0829[h]	146	55.8	24.5	34.8	141	0.076	0.105	0.196	0.080
2-Chloro-2-methylpropane	50.8	240	0.0737[h]	147	57.0	37.4	52.3	168	0.134	0.183	0.279	0.010
1-Chlorobutane	77.5	80.0	0.0745[h]	145	55.8	72.3	88.1	145	0.265	0.317	0.391	0.008
2-Chloro-2-methylbutane	85.7	60.3	0.0675[h]	148	57.0	58.8	79.3	194	0.243	0.320	0.439	-
1-Chloropentane	108.4	23.9	0.0681[h]	147	56.8	74.7	96.6	197	0.310	0.392	0.505	-
Chlorocyclopentane	113	-	0.0718	146	55.6	77.5	106	211	0.322	0.429	0.562	0.050
Chlorobenzene	132	9.11	0.0747	146	55.8	107	131	205	0.478	0.574	0.688	-
1-Chlorohexane	134.5	7.15	0.0631[h]	150	55.8	77.3	95.8	189	0.370	0.449	0.591	0.013
o-Chlorotoluene	159.2	2.66	0.0688	146	55.5	102	122	192	0.514	0.605	0.741	0.005
1-Chloroheptane	159.2	2.2	0.0591[h]	150	55.5	81.5	101	143	0.437	0.531	0.625	0.013
3-(Chloromethyl) heptane	172.	-	0.0557[h]	148	55.7	63.4	80.5	183	0.374	0.465	0.614	0.032

TABLE I (Continued)

Solvent	BP (C°)	Vapor pressure at 20°C (Torr)	Diffusion coefficient at 25°C (cm^2/sec)	Volume charcoal (ml)[a]	Weight charcoal (g)[b]	Experimental breakthrough times			Wt. solvent adsorbed per wt. of carbon			Weight water adsorbed at $t_{100\%}$ per wt. carbon[f] (g/g)
						$t_{1\%}$ (min)	$t_{10\%}$ (min)	$t_{99\%}$ (min)	$t_{1\%}$[c] (g/g)	$t_{10\%}$[d] (g/g)	t_{100}[e] (g/g)	
Dichlorides[g]												
Dichloromethane	40.2	346	0.1037	144	55.4	10.1	15.8	63.7	0.034	0.052	0.101	0.132
trans-1,2-Dichloroethylene	49	263	0.0828[h]	145	55.7	33.0	50.3	124	0.127	0.187	0.268	0.065
1,1-Dichloroethane	56.5	158	0.0919	143	55.5	23.3	40.1	225	0.092	0.152	0.327	0.034
cis-1,2-Dichloroethylene	59.8	142	0.0828[h]	144	55.3	29.8	42.6	165	0.116	0.160	0.298	0.063
1,2-Dichloroethane	83.5	60.2	0.0907	144	55.3	54.0	79.7	186	0.214	0.305	0.456	0.036
1,2-Dichloropropane	96.4	42.3	0.0794	145	55.8	65.0	90.3	200	0.291	0.393	0.554	0.034
cis,trans-1,3-Dichloropropene	108	-	0.0763[h]	147	56.7	85.5	110	208	0.319	0.402	0.606	0.036
1,4-Dichlorobutane	162	3.10	0.0666[h]	146	55.6	108	129	215	0.505	0.637	0.755	-
o-Dichlorobenzene	180.4	0.86	0.0646[h]	146	57.3	109	132	239	0.618	0.736	0.911	-
Trichlorides[g]												
Chloroform	61.2	159.3	0.0888	144	55.6	33.2	52.4	174	0.158	0.240	0.415	0.050
Methyl chloroform	74	105	0.0794	144	56.2	40.4	58.9	197	0.212	0.299	0.530	0.036
Trichloroethylene	86.5	58.6	0.0875	145	54.8	55.3	83.0	195	0.293	0.428	0.625	0.038
1,1,2-Trichloroethane	113.6	17.5	0.0792	145	56.1	71.8	112	206	0.377	0.568	0.773	0.043
1,2,3-Trichloropropane	156	2.1	0.0672[h]	147	56.2	111	132	223	0.643	0.754	0.915	-

TABLE I (continued)

Solvent	BP (C°)	Vapor pressure at 20°C (Torr)	Diffusion coefficient at 25°C (cm^2/sec)	Volume charcoal (ml)[a]	Weight charcoal (g)[b]	Experimental breakthrough times $t_{1\%}$ (min)	$t_{10\%}$ (min)	$t_{99\%}$ (min)	Wt. solvent adsorbed per wt. of carbon $t_{1\%}$[c] (g/g)	$t_{10\%}$[d] (g/g)	$t_{100\%}$[e] (g/g)	Weight water adsorbed at $t_{100\%}$ per wt. carbon[f] (g/g)
Tetrachlorides[g]												
Carbon tetrachloride	76.8	92.1	0.0828	144	55.4	77.0	90.0	147	0.473	0.545	0.677	
Perchloroethylene	121.2	14.0	0.0797	146	55.7	107	129	209	0.704	0.835	1.01	
1,1,2,2-Tetrachloroethane	146	4.73	0.0722	146	55.3	104	131	216	0.809	0.861	1.07	
Pentachlorides[g]												
Pentachloroethane	161	-	0.0673	145	56.1	93.0	117	187	0.742	0.914	1.13	
Acetates[g]												
Methyl acetate	57.3	170.2	0.0978	146	55.6	32.8	46.5	143.8	0.097	0.133	0.214	0.073
Vinyl acetate	72.5	91.2	0.0793[h]	148	55.6	55.0	81.1	235	0.188	0.269	0.391	0.006
Ethyl acetate	72.2	74.4	0.0861	145	60.6	66.8	84.7	172	0.215	0.267	0.350	0.008
Isopropyl acetate	87.5	47.3	0.0770	146	55.6	64.5	85.6	166	0.262	0.339	0.453	0.036
Isopropenyl acetate	96	30.0	0.0718[h]	145	57.1	80.6	106	193	0.323	0.409	0.507	
Propyl acetate	101.3	24.9	0.0768	145	55.9	78.8	99.0	164	0.318	0.392	0.507	0.020
Allyl acetate	103.5	-	0.0718[h]	148	56.1	75.8	95.6	246	0.299	0.369	0.517	0.043
sec-Butyl acetate	111.5	-	0.0648	145	55.9	82.8	101	164	0.381	0.456	0.537	-
Butyl acetate	126.1	8.0	0.0672	148	55.0	77.3	96.9	228	0.361	0.443	0.595	0.023
Isopentyl acetate	141.5	3.8	0.0603[h]	148	55.8	70.9	88.3	177	0.366	0.447	0.584	0.020

TABLE I (continued)

Solvent	BP (C°)	Vapor pressure at 20°C (Torr)	Diffusion coefficient at 25°C (cm^2/sec)	Volume charcoal (ml)[a]	Weight charcoal (g)[b]	Experimental breakthrough times			Wt. solvent adsorbed per wt. of carbon			Weight water adsorbed at $t_{100\%}$ per wt. carbon[f] (g/g)
						$t_{1\%}$ (min)	$t_{10\%}$ (min)	$t_{99\%}$ (min)	$t_{1\%}$ (g/g)[c]	$t_{10\%}$ (g/g)[d]	$t_{100\%}$ (g/g)[e]	
Acetates[g] Cont.												
1,3-Dimethylbutyl acetate	146.2	4	0.0567[h]	149	55.8	60.6	76.0	188	0.346	0.426	0.588	0.025
Pentyl acetate	148.4	2.95	0.0610	148	55.7	72.6	87.3	225	0.375	0.444	0.616	0.014
Hexyl acetate	169	-	0.0567[h]	148	55.5	67.0	85.3	202	0.385	0.480	0.658	-
Ketones[i]												
Acetone	56.2	307	0.1049	164	60.8	37.1	46.0	119	0.078	0.095	0.135	0.109
2-Butanone	79.6	70.6	0.0903	160	66.0	81.9	94.4	239	0.198	0.225	0.295	0.056
2-Pentanone	102.3	30.5	0.0793	159	58.0	104	121	231	0.341	0.392	0.483	0.016
3-Pentanone	102.7	26.8	0.0740[h]	162	58.4	93.5	114	175	0.305	0.365	0.449	0.055
4-Methyl-2-pentanone	115.5	16	0.0677[h]	160	58.1	96.1	111	211	0.367	0.418	0.511	0.007
Mesityl oxide	129.7	7.9	0.0760	169	60.2	122	139	224	0.440	0.495	0.578	-
Cyclopentanone	130.7	-	0.0796[h]	167	64.3	141	161	308	0.408	0.460	0.585	-
2,4-Pentanedione	140.4	6.5	0.0727[h]	176	70.6	130	114	214	0.408	0.447	0.527	0.009
3-Heptanone	147.3	-	0.0628[h]	160	58.1	91.0	105	186	0.396	0.451	0.548	0.014
2-Heptanone	151.2	2.8	0.0628[h]	187	61.9	101	114	237	0.412	0.460	0.560	0.005
Cyclohexanone	155.6	3.4	0.0729[h]	166	64.7	126	144	249	0.423	0.477	0.585	0.003
5-Methyl-3-heptanone	159.5	-	0.0588[h]	165	62.9	86.4	99.3	183	0.389	0.442	0.550	0.024

TABLE I (Continued)

Solvent	BP (C°)	Vapor pressure at 20°C (Torr)	Diffusion coefficient at 25°C (cm^2/sec)	Volume charcoal (ml)[a]	Weight charcoal (g)[b]	Experimental breakthrough times			Wt. solvent adsorbed per wt. of carbon			Weight water adsorbed at $t_{100\%}$ per wt. carbon[f] (g/g)
						$t_{1\%}$ (min)	$t_{10\%}$ (min)	$t_{99\%}$ (min)	$t_{1\%}$[c] (g/g)	$t_{10\%}$[d] (g/g)	$t_{100\%}$[e] (g/g)	
<u>Ketones[i] Cont.</u>												
3-Methyl-cyclohexanone	168	-	0.0669[h]	162	63.5	101	123	216	0.395	0.472	0.595	-
Diisobutyl ketone	169.4	-	0.0554[h]	162	60.4	70.8	83.3	171	0.369	0.427	0.556	0.005
4-Methylcyclo-hexanone	171.3	-	0.0669[h]	172	67.9	111	126	245	0.463	0.520	0.580	0.009
<u>Alkanes[i]</u>												
Pentane	36.1	424	0.0842	166	62.6	60.7	71.3	147	0.155	0.179	0.228	0.020
2,3-Dimethylbutane	58.0	191	0.0689[h]	167	63.5	72.0	81.1	192	0.216	0.241	0.300	0.021
Hexane	68.7	121	0.0732[h]	160	55.0	52.3	64.6	178	0.181	0.220	0.334	0.036
Methylcyclopentane	71.8	110	0.0734[h]	164	66.7	62.2	76.1	174	0.174	0.209	0.278	0.036
Cyclohexane	80.7	77.5	0.0743[h]	161	59.3	68.7	82.3	179	0.216	0.254	0.337	0.024
Cyclohexene	83.3	70.4	0.0765[h]	159	57.3	85.8	100	193	0.272	0.313	0.401	-
2,2,4-Trimethyl-pentane	96.5	38.6	0.0594[h]	161	57.5	68.3	80.4	166	0.300	0.348	0.440	0.019
Heptane	98.5	35.4	0.0636[h]	160	57.9	78.2	89.8	188	0.299	0.339	0.432	0.019
Methylcyclohexane	100.9	36.2	0.0679[h]	160	57.5	68.5	80.5	191	0.259	0.300	0.440	0.045

TABLE I (Continued)

Solvent	BP (C°)	Vapor pressure at 20°C (Torr)	Diffusion coefficient at 25°C (cm^2/sec)	Volume charcoal (ml)[a]	Weight charcoal (g)[b]	Experimental breakthrough times			Wt. solvent adsorbed per wt. of carbon			Weight water adsorbed at $t_{100\%}$ per wt. carbon[f] (g/g)
						$t_{1\%}$ (min)	$t_{10\%}$ (min)	$t_{99\%}$ (min)	$t_{1\%}$[c] (g/g)	$t_{10\%}$[d] (g/g)	$t_{100\%}$[e] (g/g)	
Alkanes[i] Cont.												
1,3,5-Cycloheptatriene	115.5	-	0.0742[h]	168	63.4	121	137	246	0.389	0.435	0.536	0.003
2,2,5-Trimethylhexane	124.5	12.5	0.0559[h]	166	64.2	67.6	80.0	168	0.266	0.310	0.444	0.001
5-Ethylidene-2-norbornene	147.5	4.2	0.0644[h]	165	67.4	86.5	101	221	0.341	0.393	0.526	0.007
Cyclooctane	150	-	0.0639[h]	172	70.3	96.8	113	220	0.345	0.397	0.497	0.027
Nonane	150	3.15	0.0559[h]	168	63.5	76.2	89.3	198	0.340	0.393	0.490	
Decane	174	0.96	0.0530[h]	164	57.7	70.8	81.5	158	0.386	0.439	0.553	0.017
Amines[i]												
Methylamine	-6.7	2160	0.1300[h]	161	58.5	12.4	17.9	91.5	0.015	0.020	0.041	0.150
Dimethylamine	6.7	1285	0.1023[h]	164	70.0	17.1	21.7	94	0.024	0.030	0.050	0.291
Ethylamine	16.6	872	0.1032[h]	161	59.8	40.5	49.7	270	0.068	0.081	0.179	0.268
Isopropylamine	31.5	478	0.0879[h]	160	60.4	65.6	75.8	194	0.142	0.162	0.275	0.136
Propylamine	47.8	247	0.0879[h]	172	65.5	90.0	111	330	0.180	0.217	0.335	0.252
Diethylamine	55.5	188	0.0993	160	62.1	88.0	105	213	0.229	0.269	0.351	0.100
Butylamine	77.5	75	0.0872	162	63.9	110	125	278	0.278	0.312	0.429	0.031
Triethylamine	89.4	46.2	0.0754	160	59.1	81.1	91.0	174	0.307	0.341	0.426	0.032
Dipropylamine	110	18.2	0.0647[h]	170	68.2	93.0	105	226	0.305	0.340	0.439	0.060
Diisopropylamine	110.5	-	0.0647[h]	171	67.0	77.0	87.1	185	0.257	0.288	0.370	0.069

TABLE I (continued)

Solvent	BP (C°)	Vapor pressure at 20°C (Torr)	Diffusion coefficient at 25°C (cm^2/sec)	Volume charcoal (ml)^a	Weight charcoal (g)^b	Experimental breakthrough times			Wt. solvent adsorbed per wt. of carbon			Weight water adsorbed at $t_{100\%}$ per wt. carbon^f (g/g)
						$t_{1\%}$ (min)	$t_{10\%}$ (min)	$t_{99\%}$ (min)	$t_{1\%}$^{c} (g/g)	$t_{10\%}$^{d} (g/g)	$t_{100\%}$^{e} (g/g)	
Amines[i] Cont.												
Cyclohexylamine	134	-	0.0664[h]	169	64.3	112	128	279	0.382	0.431	0.564	0.141
Dibutylamine	159	1.61	0.0567[h]	164	64.6	75.5	84.8	186	0.335	0.372	0.480	0.009
Miscellaneous												
Methyl iodide[i]	42.4	336	0.0900[h]	160	58.2	11.6	17.7	94.5	0.063	0.092	0.187	0.223
Acrylonitrile[i]	77.3	67.8	0.1059	160	58.0	48.5	61.1	168	0.098	0.121	0.174	0.016
Dibromomethane[i]	98.6	33	0.0826	160	62.8	82	121	279	0.502	0.717	1.06	0.006
Pyridine[i]	115.2	15.4	0.0824[h]	160	64.3	119	134	292	0.324	0.360	0.460	0.076
Epichlorohydrin[g]	116.9	12.5	0.0821[h]	146	56.9	85.5	110	288	0.308	0.387	0.566	0.014
2-Methoxyethanol[g]	124.4	9.0	0.0884	146	55.5	116	145	249	0.352	0.431	0.540	0.096
1,2-Dibromoethane[i]	131.5	8.6	0.0840[h]	161	61.9	141	165	303	0.946	1.09	1.336	-
1-Nitropropane[i]	131.6	7.2	0.0781[h]	160	63.2	143	164	322	0.443	0.504	0.638	-
2-Ethoxyethanol[g]	135.5	-	0.0788	148	55.4	77.0	123	283	0.277	0.426	0.593	0.011
Acetic anhydride	139.6	3.7	0.0755[h]	161	61.0	124	138	200	0.459	0.506	0.592	0.070

TABLE I (Continued)

Solvent	BP (C°)	Vapor pressure at 20°C (Torr)	Diffusion coefficient at 25°C (cm^2/sec)	Volume charcoal (ml)[a]	Weight charcoal (g)[b]	Experimental breakthrough times			Wt. solvent adsorbed per wt. of carbon			Weight water adsorbed at $t_{100\%}$ per wt. carbon[f] (g/g)
						$t_{1\%}$ (min)	$t_{10\%}$ (min)	$t_{99\%}$ (min)	$t_{1\%}$[c] (g/g)	$t_{10\%}$[d] (g/g)	$t_{100\%}$[e] (g/g)	
Miscellaneous Cont.												
2-Methoxyethyl-acetate[g]	144.5	3.6	0.0666[h]	150	55.7	93.3	113.2	303	0.438	0.521	0.707	-
Bromobenzene[i]	156	3.0	0.0661[h]	160	58.1	142	159	297	0.849	0.940	1.126	-
2-Ethoxyethyl acetate[g]	156.3	2.0	0.0619[h]	148	55.8	79.5	96.5	248	0.417	0.497	0.689	0.010

---

[a] Average volumes for a cartridge pair are 146.3 ± 1.9 ml for the Type 1 and 163.8 ± 4.3 ml for the Type 2.

[b] Average weights for a cartridge pair are 56.1 ± 1.2 g for the Type 1 and 62.2 ± 3.9 g for the Type 2.

[c] Calculated from $W_{1\%} = t_{1\%}\ MQC/24.1\quad 10^6\ W_c$.

[d] Estimated from $W_{10\%} = [t_{1\%} + 0.9\ (t_{10\%} - t_{1\%})]\ [MQC]/24.1\quad 10^6\ W_c$.

[e] See Ref. 4, "Data Processing," calculation of W_s.

[f] Calculated from $W_{H_2O} = W_{total} - W_s$.

[g] Used Type 1 cartridges.

[h] Calculated from Gilliland's equation $D_{25} = [0.0043T^{1.5}(1/M_{air} + 1/M_{vap})^{0.5}]/(v_{air}^{0.33} + v_{vap}^{0.33})^2 P$, where v_{air} is 29.9 ml/mol and v_{vap} is calculated from the LeBas approximation (see Ref. 7).

[i] Used Type 2 cartridges.

to the upstream concentration) for each solvent is shown as a function of time. These figures yield the complete adsorption history from initial breakthrough to total cartridge saturation for each of the solvents and gases tested.

Table I helps summarize the data shown in Figs. 4 through 13. Here solvents are arranged by classes, and within classes by boiling point, with the most volatile compound shown first. The times to reach 1%, 10%, and 99% breakthrough and the respective weights adsorbed are shown for each solvent.

This table shows that, within each class of solvent, the most volatile solvent breaks through first. As the boiling points of the solvents within a class increase, however, the trend eventually reverses. At some point the breakthrough time actually *decreases* with rising solvent boiling points. This occurs for each class of solvent.

Table I also illustrates how the weight of solvent adsorbed varies with the vapor pressure as well as the boiling point. Within each solvent class the weight adsorbed is both an increasing function of the boiling point and a decreasing function of the vapor pressure—the two being interrelated. This is shown to be the case for 1%, 10%, and 100% breakthrough. These data can be used, therefore, to approximate the weight adsorbed of an untested solvent once its class and boiling point or vapor pressure are known.

Table I also gives the diffusion coefficients and the activated carbon weights and volumes needed in the theoretical calculation of the breakthrough times. It also shows the weights of water adsorbed. Note the relatively large amount of water adsorbed in connection with more volatile solvents, especially those that are miscible with water.

Calculation of Breakthrough Times

The ability to predict the cartridge breakthrough mathematically for any solvent that may be encountered would be useful. Initial cartridge breakthrough can be calculated from

$$t_b = \frac{10^6 V_m w W_c}{MQC} \qquad (1)$$

where t_b = initial cartridge breakthrough time (min).
V_m = molar volume at the system temperature and pressure (24.1 liters/mole at 20°C, 760 torr).
w = weight of solvent adsorbed per gram of activiated carbon (gm/gm).
W_c = weight of activated carbon (gm).
M = molecular weight of the contaminant (gm/mole).
Q = airflow rate (liters/min).
C = upstream gas concentration (ppm).

All the terms can be measured or calculated except w. The weight of solvent adsorbed is extremely difficult to predict, since it is a complex function of the nature of the adsorbent and solvent vapor. Therefore, equation 1 is useful only if the weight is determined experimentally. Estimations of the breakthrough time can be calculated, however, from the adsorption isotherm and the Mecklenburg equation.

The adsorption isotherm for microporous adsorbents yields the maximum weight of solvent adsorbed at total carbon saturation and can be calculated by

$$w_s = \rho W_0 \exp\left\{\frac{-BT^2}{\beta^2}[\log(p_s/p)]^2\right\} \qquad (2)$$

where w_s = equilibrium static adsorptive capacity per unit weight carbon (gm/gm).
ρ = density of solvent (gm/cm^3).
W_0 = total volume of adsorption space (cm^3/gm).
B = microporosity constant for the carbon.
T = temperature (°K).
β = affinity coefficient of solvent vapor for the activated carbon.

and standard solvent (calculated from Sugden's equation).

p, p_s = solvent density for the unknown and standard solvent (gm/cm^3).

M, M_s = molecular weights for the unknown and standard solvent (gm/mole).

All the parameters needed to solve the adsorption isotherm are given in Tables I through V. Comparison of the actual experimental values of w_s are also shown in Tables IV and V. Note that the more volatile materials show the greatest deviation from the calculated values. This is due primarily to the preferential adsorption of the water vapor present. In theory, the adsorption isotherm described by equation 2 is valid only for a single vapor in air; it neglects competing adsorption by water or any other vapors. Even by expanding the adsorption isotherm to include multiple vapor systems, it is still difficult to predict to what extent highly polar materials such as

TABLE IV
Comparison of Calculated and Observed Adsorption Capacity of Type 1 Cartridges for Several Solvents[a]

		Adsorptive Capacity, w_s		
Solvent	Affinity Coefficient, β	Observed (gm/gm)	Calculated from Equation 2 (gm/gm)	Deviation from Observed (%)
Benzene	1.00[b]	0.327	0.408	+ 25
Toluene	1.33[b]	0.473	0.507	+ 7.2
m-Xylene	1.38[c]	0.536	0.540	+ 0.7
Methanol	0.40[b]	0.018	0.048	+167
Ethanol	0.61[b]	0.168	0.251	+ 49
Propanol	0.84[d]	0.384	0.429	+ 12
n-Butanol	1.02[d]	0.512	0.495	− 3.3
n-Pentanol	1.22[d]	0.552	0.525	− 4.9
Methyl chloride	0.56[b]	0.008	0.016	+100
Ethyl chloride	0.76[b]	0.048	0.129	+169
1-Chloropropane	0.91[c]	0.196	0.293	+ 49
1-Chlorobutane	1.09[c]	0.391	0.426	+ 9.0
Chlorobenzene	1.18[c]	0.562	0.669	+ 19
Dichloromethane	0.66[b]	0.101	0.216	+114
1,2-Dichloroethane	0.90[c]	0.456	0.555	+ 22
1,4-Dichlorobutane	1.28[c]	0.755	0.720	− 4.6
o-Dichlorobenzene	1.36[c]	0.911	0.851	− 6.6
Chloroform	0.86[b]	0.415	0.518	+ 25
1,1,2-Trichloroethane	1.08[c]	0.773	0.822	+ 6.3
Carbon tetrachloride	0.96[b]	0.677	0.690	+ 1.9
Perchloroethylene	1.21[c]	1.01	0.965	− 4.5
Methyl acetate	0.89[d]	0.214	0.333	+ 56
Ethyl acetate	1.10[d]	0.350	0.442	+ 26
Propyl acetate	1.30[d]	0.507	0.513	+ 1.2
Butyl acetate	1.48[d]	0.584	0.550	− 5.8
Pentyl acetate	1.63[d]	0.616	0.577	− 6.3

[a] The equilibrium partial pressure, p, at 1000 ppm is 0.76 torr. The saturated vapor pressure, p_s, is taken from Table I.

[b] Experimental values taken from ref. 6.

[c] Calculated from parachors using Sugden's equation.

[d] Calculated from equation 3 using molar volumes.

water will interfere with the normal adsorption processes of organic vapors. Currently there is no satisfactory method of correction for this interference.[6,8]

As was previously mentioned, w_s is the weight adsorbed at *total* saturation—that is, at 100% breakthrough. Initial breakthrough, however, occurs long before the equilibrium adsorptive capacity is established. Nevertheless, such breakthrough times can be estimated from the Mecklenburg equation once w_s has been determined.

The Mecklenburg equation states that

$$t_b = \frac{w_s \rho_c A n}{Q C_0}\left[z + \frac{1}{a_c \rho_c}\left(\frac{dG}{n}\right)^{0.41}\left(\frac{n}{\rho_a D_{20}}\right)^{0.67} \ln(C_b/C_I)\right] \quad (4)$$

where

$$C_o = \frac{MC_I}{24.1 \times 10^6}$$

$$G = \frac{1000 \rho_a Q V_v \rho_c}{60 A n}$$

$$z = V/A$$

$$D_{20} = 0.967 D_{25}$$

and ρ_c = carbon density (gm/cm³).
A = cross-sectional area of the adsorbent bed (cm²).
V = carbon volume (cm³).
n = number of cartridges tested.
C_0 = assault concentration (gm/liter).
z = bed depth (cm).
a_c = specific surface area (cm²/gm).
d = diameter of granule (cm).
G = mass velocity through cartridge (gm/cm²-sec).
n = viscosity of the air–gas stream (gm/cm-sec).
ρ_a = density of air-vapor stream (gm/cm³).
D = diffusion coefficient (cm²/sec).
C_b = breakthrough concentration (ppm).
C_I = assault concentration (ppm).
V_v = void volume (cm³/gm).

Equation 4 is generally useful only for $C_b/C_I < 0.2$—that is, for breakthroughs

TABLE V
Comparison of Calculated and Observed Adsorption Capacity of Type 2 Cartridges for Several Solvents[a]

Solvent	Affinity Coefficient, β	Adsorptive Capacity, w_s: Observed (gm/gm)	Adsorptive Capacity, w_s: Calculated from Equation 2 (gm/gm)	Deviation from Observed (%)
Acetone	0.88[b]	0.135	0.236	+75
2-Butanone	1.10[c]	0.295	0.360	+22
2-Pentanone	1.19[c]	0.483	0.427	−12
2-Heptanone	1.57[c]	0.560	0.493	−12
Pentane	1.08[b]	0.228	0.225	− 1.3
Hexane	1.295[b]	0.334	0.319	− 4.5
Heptane	1.46[b]	0.432	0.375	−13
Nonane	1.85[d]	0.490	0.434	−11
Decane	2.05[d]	0.553	0.442	−20
Methylamine	0.72[d]	0.041	0.061	+49
Ethylamine	0.91[d]	0.179	0.166	− 7.3
Butylamine	1.29[d]	0.429	0.371	−14
Dibutylamine	1.25[d]	0.480	0.466	− 2.9

[a] The equilibrium partial pressure, p, at 1000 ppm is 0.76 torr. The saturated vapor pressure, p_s, is taken from Table I.

[b] Experimental values taken from ref. 6.

[c] Calculated from equation 3 using molar volumes.

[d] Calculated from parachors using Sugden's equation.

less than 20%.

The predicted and actual breakthrough times are compared in Table VI and VII. In general, the predicted times are somewhat more optimistic than those determined experimentally. This again can be explained by water's tendency to occupy the available adsorption sites.

Tables VI and VII show conclusively that approximate breakthrough times can indeed be calculated, but only if the activated carbon is well characterized. Approximately twenty-five variables must be known, however, before such calculations can be initiated.

There have been attempts to simplify these calculations by relating the breakthrough time or weight adsorbed directly to a single property of the solvent such as boiling point, molecular weight, vapor pressure, or diffusion coefficient. These oversimplifications generally fail, however, since so many interrelated variables play a role in adsorption.

Effect of Concentration

In a preliminary investigation we varied the concentration, from 125 to 2000 ppm for

TABLE VI
Comparison of Predicted and Actual 1% Breakthrough Times, Type 1 Cartridges[a]

Material	Time Measured (min)	Calculated from Mecklenburg Equation: Using Experimental Weight Adsorbed (min)	Calculated from Mecklenburg Equation: Using Calculated Weight Adsorbed from Adsorption Isotherm (min)
Benzene	73.3	74.2	92.6
Toluene	94.3	89.1	95.5
m-Xylene	98.7	82.0	82.6
Methanol	0.2	10.9	29.1
Ethanol	28.0	67.6	101
n-Propanol	70.4	115	128
n-Butanol	115	120	116
n-Pentanol	102	104	99.2
Methyl chloride	0.05	3.0	5.9
Ethyl chloride	5.6	13.2	35.6
1-Chloropropane	24.5	43.0	64.3
1-Chlorobutane	72.3	70.8	77.1
Chlorobenzene	107	83.8	99.7
Dichloromethane	10.6	21.6	46.2
1,2-Dichloroethane	54.0	81.2	98.8
1,4-Dichlorobutane	108	96.4	91.9
o-Dichlorobenzene	109	99.6	93.0
Chloroform	33.2	61.0	76.1
1,1,2-Trichloroethane	71.8	98.7	105
Carbon tetrachloride	77.0	75.8	77.3
Perchloroethylene	107	104	99.3
Methyl acetate	32.8	51.7	80.5
Ethyl acetate	66.8	69.1	87.3
n-Propyl acetate	78.8	83.9	84.9
n-Butyl acetate	77.3	81.8	77.0
n-Pentyl acetate	72.6	74.5	69.8

[a] Test conditions; 53.3 liters/min, 50% relative humidity, and 20°C. Cartridge characteristics are summarized in Tables II and III.

TABLE VII
Comparison of Predicted and Actual 1% Breakthrough Times, Type 2 Cartridges

		Calculated from Mecklenburg Equation	
Material	Time Measured (min)	Using Experimental Weight Adsorbed (min)	Using Calculated Weight Adsorbed from Adsorption Isotherm (min)
Acetone	37.1	58.3	102
2-Butanone	81.9	101	123
2-Pentanone	104	137	121
2-Heptanone	101	116	102
n-Pentane	60.7	77.6	76.6
n-Hexane	52.3	93.7	89.5
n-Heptane	78.2	103	89.1
n-Nonane	76.2	89.4	79.2
n-Decane	70.8	90.3	72.2
Methylamine	12.4	33.6	50.0
Ethylamine	40.5	99.3	92.1
n-Butylamine	110	145	125
Di-*n*-butlyamine	75.5	86.9	84.4

[a] Test conditions; 53.3 liters/min, 50% relative humidity, and 20°C. Cartridge characteristics are summarized in Tables II and III.

benzene and from 50 to 2000 ppm for acetone, and measured the effect on service life. The characteristic S-shaped breakthrough curves for these solvents appear in Figures 14 and 15. Although the time to reach a given breakthrough increases as the concentration diminishes, the breakthrough time–concentration relationship is not inversely proportional as one might intuitively suspect. However, a logarithmic plot of the breakthrough time (for example, at 10%) as a function of the concentration yields the linear relationship shown in Figure 16. The resultant empirical equations for the straight lines are:

$t_{10\ \text{percent}} = 1.4 \times 10^4 \times C_I^{-0.76}$ for benzene

$t_{10\ \text{percent}} = 1.1 \times 10^3 \times C_I^{-0.46}$ for acetone

where $t_{10\ \text{percent}}$ is the time in minutes to achieve a 10% breakthrough, and C_I is the upstream assault concentration in parts per million. These results conform to the basic Freundlich equation and have been demonstrated previously by Fraust and Hermann.[9]

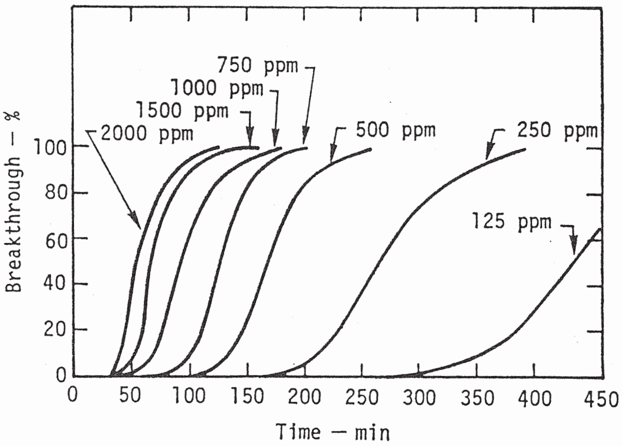

Figure 14. Breakthrough curves for type 1 cartridges, at various concentations of benzene. Each cartridge pair contained 56.6 ± 1.5 gm of activated carbon and was tested at a flow rate of 53.3 liters/min and 50% relative humidity.

Summary

We have examined the service lives of organic vapor respirator cartridges exposed to aromatics, alcohols, acetates, alkanes, ketones, amines, and chlorinated materials. We assaulted the cartridges under standardized conditions and monitored the downstream concentration to cartridge saturation. The standard test conditions included a sol-

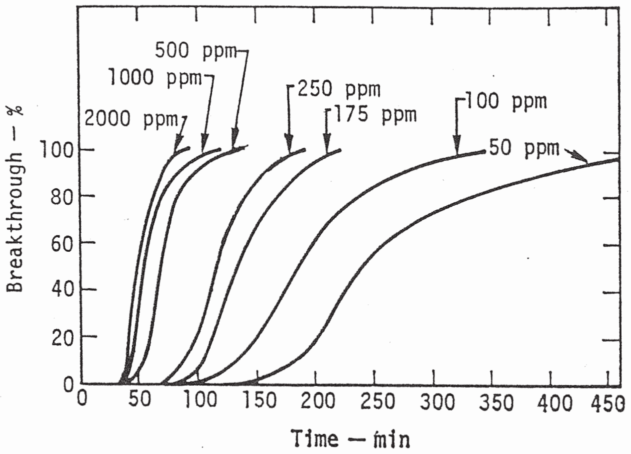

Figure 15. Breakthrough curves for type 2 cartridges at various concentrations of acetone. Each cartridge pair contained 60.5 ± 2.9 gm of activated carbon and was tested at a flow rate of 53.3 liters/min and 50% relative humidity.

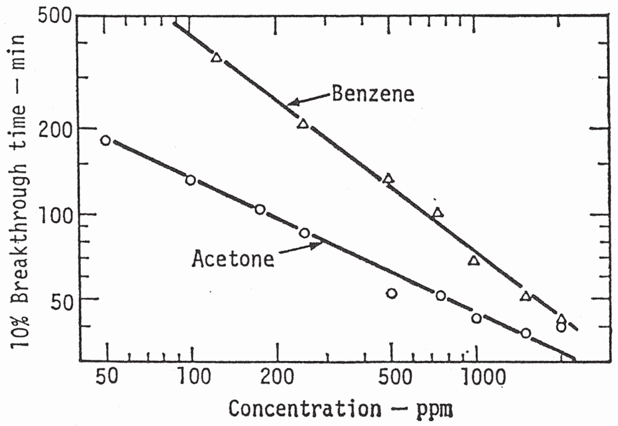

Figure 16. The 10% breakthrough time as a function of concentration for benzene and acetone.

vent concentration of 1000 ppm, 50% relative humidity, and a flow of 53.3 liters/min.

Measured breakthrough times agreed reasonably with calculated values obtained from the adsorption isotherm and Mecklenburg equation. In general, the activated carbon has a greater affinity for the less volatile materials.

The relative humidity greatly influences the amount of solvent vapor adsorbed, significantly decreasing the activated carbon's affinity for volatile or water-soluble solvents.

A brief investigation showed that the effect of concentration on breakthrough time conforms to the basic Freundlich equation.

References

1. Ruch, W. E., G. O. Nelson, C. L. Lindeken, R. E. Johnsen, and D. J. Hodgkins: Respirator Cartridge Efficiency Studies: I. Experimental Design, *Amer. Ind. Hyg. Ass. J. 33:* 105 (1972).
2. Nelson, G. O., and D. H. Hodgkins: Respirator Cartridge Efficiency Studies: II. Preparation of Test Atmospheres. *Amer. Ind. Hyg. Ass. J. 33:*110 (1972).
3. Nelson, G. O., R. E. Johnsen, C. L. Lindeken, and R. D. Taylor: Respirator Cartridge Efficiency Studies: III. A Mechanical Breathing Machine to Simulate Human Respiration. *Amer. Ind. Hyg. Ass. J. 33:*745 (1972).
4. Nelson, G. O., and C. A. Harder: Respirator Cartridge Efficiency Studies: IV. Effects of Steady-State and Pulsating Flow. *Amer. Ind. Hyg. Ass. J. 33:*797 (1972).
5. Smisek, M., and S. Cerny: *Active Carbon,* pp. 133-135, Elsevier, New York (1970).
6. Freedman, R. W., B. I. Ferber, and A. M. Hartstein: Service Lives of Respirator Cartridges Versus Several Classes of Organic Vapors. *Amer. Ind. Hyg. Ass. J. 34:*55 (1973).
7. Perry. J. H. (ed.): *Chemical Engineers' Handbook,* 3rd ed. pp. 538-539, McGraw-Hill, New York (1950).
8. Walker, P. L. (ed.): *Chemistry and Physics of Carbon,* pp. 115-116, Dekker, New York (1966).
9. Fraust, C. L., and E. R. Hermann: The Adsorption of Aliphatic Acetate Vapors onto Activated Carbon. *Amer. Ind. Hyg. Ass. J. 30:* 494 (1969).

資料 10

産業医学 35巻，*Jpn J Ind Health*, Vol. 35, 1993

短　報

有機溶剤蒸気46種類に対する有機ガス用吸収缶の破過時間

Service Lives of Respirator Cartridges for 46 Organic Solvent Vapors

Key words: respirator cartridge; breakthrough time; organic solvent; boiling point

有機溶剤中毒予防規則では第1種有機溶剤7物質，第2種有機溶剤40物質を対象とし，作業者がこれらの有機溶剤蒸気に高濃度曝露の危険性がある作業では有機ガス用吸収缶（以下，吸収缶と略す）を装備した防毒マスクを装着するように指導されている．この吸収缶の除毒能力は一定量の有機溶剤蒸気を吸着すると，吸収缶の気流出口側に漏洩してくる破過と呼ぶ現象が起きることをもとに判断している1)．作業者は，この吸収缶の破過が生じる前に新しい吸収缶と交換する必要がある．有機溶剤中毒の災害事例では，吸収缶の破過を知らずに使用し中毒を起こした事例が昭和63年2例，平成元年3例，平成2年3例，平成3年2例2) 報告されている．この数値は労働省に報告された災害事例であり中毒の発現はないまでも，かなりの作業者が吸収缶の吸着能力を超過して使用していることが危惧される．吸収缶の有機溶剤蒸気に対する吸着性能は四塩化炭素蒸気について破過曲線が付記されているのみで，その他の有機溶剤蒸気に対する破過試験の結果がないことも大きな原因と考えられる．本研究では有機溶剤中毒予防規則の第1種および第2種有機溶剤のうち，クレゾールを除く46物質を対象に吸収缶の破過試験を行い，比較検討した．

実験方法

1.　使用吸収缶：吸収缶は，三光化学工業製直結式小型吸収缶 G-31（活性炭充塡量 22 g）を用いた．

2.　試験装置：吸収缶の破過試験には前報3) の装置を用いた．試験は有機溶剤蒸気濃度300 ppm，温度20℃，相対湿度50%，流量30 l/min で吸収缶に通気し，透過ガス濃度が5 ppm になるまでの時間（破過時間）を3回繰り返し実験し，平均値を求めた．そして，四塩化炭素の破過時間に対する各有機溶剤の破過時間の比率を求め，相対破過比とした．使用したガスクロマトグラフは水素炎イオン化型検出器を装備した島津製 GC-8A で，ガラス製（内径 3.2 mm，長さ 2 m）のカラムに 5% Bentone 34+5% DIDP（担体 Uniport B）を充塡した．試験溶剤は和光純薬工業（株）製および東京化成工業（株）製特級を使用した．

Table 1.　Breakthrough time and relative breakthrough time.

Organic solvent	Group	B.P.(℃)	B.T.(min)	R.B.T.
Toluene	Aromatics	110	175	1.35
Xylene		138	178	1.37
Styrene		145	207	1.59
Dichloromethane	Chlorides	40	28	0.22
Chloroform		61	96	0.74
1,2-Dichloroethylene		61	110	0.85
1,1,1-Trichloroethane		74	137	1.05
Carbon tetrachloride		76	130	1.00
1,2-Dichloroethane		83	153	1.18
Trichloroethylene		87	183	1.41
Tetrachloroethylene		121	176	1.35
Chlorobenzene		132	202	1.55
1,1,2,2-Tetrachloroethane		146	190	1.46
o-Dichlrobenzene		179	210	1.62
Methanol	Alcohols	65	3	0.02
Isopropylalcohol		82	142	1.09
2-Buthanol		100	197	1.52
Isobutylalcohol		108	194	1.49
1-Buthanol		117	223	1.72
Isopenthylalcohol		131	200	1.54
Cyclohexanol		161	156	1.20
Methylcyclohexanol		173	167	1.28
Acetone	Ketones	56	63	0.48
Methylethylketone		80	144	1.11
Methylisobutylketone		117	172	1.32
Methylbutylketone		128	152	1.17
Cyclohexanone		156	222	1.71
Methylcyclohexanone		170	172	1.32
Methyl acetate	Acetates	56	78	0.60
Ethyl acetate		77	125	0.96
Isopropyl acetate		90	145	1.12
Propyl acetate		102	157	1.21
Isobutyl acetate		117	140	1.08
Butyl acetate		127	169	1.30
Isopentyl acetate		142	144	1.11
Pentyl acetate		149	133	1.02
Methylcellosolve	Cellosolves	125	190	1.46
Cellosolve		135	210	1.62
Cellosolveacetate		156	218	1.68
Buthylcellosolve		172	250	1.92
Ethylether	Ethers	35	80	0.62
1,4-Dioxane		101	175	1.35
n-Hexane	Alkane	68	108	0.83
N,N-Dimethylformamide	Amide	153	260	2.00
Tetrahydorofuran	Furan	67	164	1.26
Carbon disulfide	Sulfide	46	50	0.38

B.P.: Boiling Point
B.T.: Breakthrough Time
R.B.T.: Relative Breakthrough Time
(B.T. of Organic Solvent ／ B.T.of Carbon Tetrachloride)

結果および考察

各種有機溶剤の破過時間，相対破過比の測定結果を Table 1 に示す．四塩化炭素の破過時間130分より短い破過時間，すなわち相対破過比が1.0より小さい有機溶剤はメタノール（相対破過比 0.02），ジクロルメタン（0.22），二硫化炭素（0.38），アセトン（0.48），酢酸メチル（0.60），エチルエーテル（0.62），クロロホルム（0.74），1,2-ジクロルエチレン（0.85），n-ヘキサン（0.83），酢酸エチル（0.96）で46有機溶剤中10物質であった．Fig. 1 は各有機溶剤の沸点（D：℃）と破過時間（T：分）の関係を示す．両者の関係は $T=1.1D+36.7$（相関係数 0.77）と良好な相関が認められ，沸点が低い有機溶剤ほど破過時間が短くなる傾向が認められた．Nelson らは121種類の有機溶剤蒸気を対象に破過試験を行い報告している4)．彼らは吸収缶の活性炭質量 56 g，溶剤蒸気濃度 1,000 ppm，温度 22℃，相対湿度 50%，流量 53.3 l/min の実験条件で破過時間を測定した．著者が行った46有機溶剤中，34有機溶剤について試験結果が報

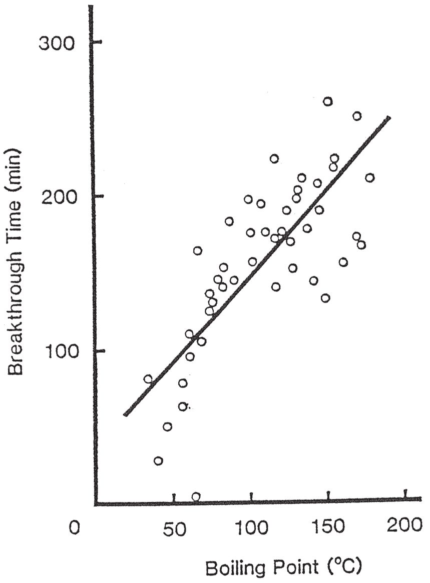

Fig. 1. Relationship between boiling points and breakthrough times for 46 organic solvents.

告されていたものの，実験条件が異なることより，そのままでは比較検討ができない．そこで，これら 34 有機溶剤について Nelson の破過時間（10% 破過）の結果より相対破過比を求めた．そして，著者と Nelson の同一溶剤における相対破過比を比較したところ，Fig. 2 に示すように，$Y=0.98X+0.14$（相関係数 0.93）となり，両者はよく対応する結果を得た．

クレゾールは蒸気圧が低く，300 ppm の有機溶剤蒸気を調製することができなかった．その他，46 有機溶剤蒸気について吸収缶に対する破過時間を測定することができた．今回の成績はこれらの有機溶剤取扱い作業場で吸収缶を使用する際の交換時期の目安になると思われる．破過時間の著しく短いメタノール，ジクロルメタン，二硫化炭素，アセトン等は吸収缶での除毒能力が低く，新たな捕集剤の開発が必要と考える．また，今回試験した以外の有機溶剤蒸気に対する破過時間は，その有機溶剤の沸点を参考にすることにより，予測が可能であることが示唆された．

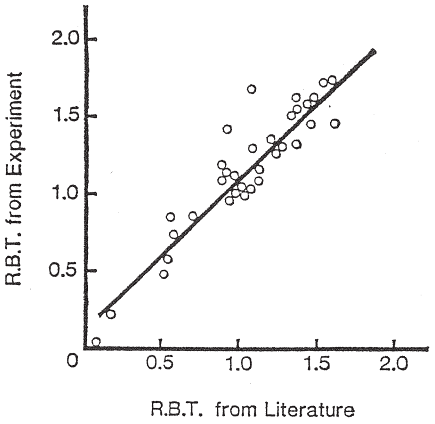

Fig. 2. Relationship between relative breakthrough times obtained from literature[4] and experiments. R.B.T.: represents relative breakthrough time.

本研究にご協力いただいた三光化学工業(株)常森和男，柳川稔両氏に深謝いたします．

文　献

1) 日本工業標準調査会．日本工業規格：ガスマスク JIS T 8152．1981：24．
2) 中央労働災害防止協会．労働衛生のしおり平成元～4 年度．1988-1992．
3) Tanaka S, Abuku S, Imaizumi S, et al. Estimation by weight increase of the service life of respirator cartridges used in a paint manufacturing plant. J Sci Labour 1990; 66: 10-15.
4) Nelson GO, Harder CA. Respirator cartridge efficiency studies: V. Effect of solvent vapor. Am Ind Hyg Assoc J 1974; 35: 391-410.

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資料 13-a

Evaluation of Carbon Tetrachloride Replacement Agents for Use in Testing Nonpowered Organic Vapor Cartridges

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Carbon tetrachloride has been used for years as a standard material for evaluating charcoal's ability to adsorb organic materials. It has also been the standard organic compound for testing organic vapor breakthrough characteristics of respirator cartridges and canisters. However, due to the potential carcinogenic characteristic of carbon tetrachloride and the lack of commercial availability, a suitable substitute organic vapor cartridge test agent is needed. Four potential replacement agents were tested (ethyl acetate, pentane, *n*-hexane, and heptane). Initially, testing was performed using the stacked-cartridge test system. This screening method identified replacement agent challenge concentrations which gave breakthrough characteristics equivalent to 1000 parts per million (ppm) carbon tetrachloride. Breakthrough time was the critical criterion. Two test conditions (550 ppm pentane and 1000 ppm n-hexane) were selected for side-by-side testing with 1000 ppm carbon tetrachloride. The results show that for the most stringent test condition ("as received" cartridges tested at 64 L/min and 80% relative humidity) the breakthrough times for two different manufacturers' organic vapor cartridges were identical for these three test conditions (1000 ppm carbon tetrachloride, 550 ppm pentane, and 1000 ppm *n*-hexane). Pentane's lower toxicity makes it the replacement agent of choice. MOYER, E.S.; PETERSON, J.A.; CALVERT, C.: EVALUATION OF CARBON TETRACHLORIDE REPLACEMENT AGENTS FOR USE IN TESTING NONPOWERED ORGANIC VAPOR CARTRIDGES. APPL. OCCUP. ENVIRON. HYG. 10(9):761–768; 1995.

The National Institute for Occupational Safety and Health (NIOSH) and the Occupational Safety and Health Administration (OSHA) have prepared and published occupational health guidelines for various chemical substances.(1) As part of the carbon tetrachloride guidelines, a special note indicates that the International Agency for Research on Cancer evaluated the data on carbon tetrachloride and concluded that it causes cancer. The American Conference of Governmental Industrial Hygienists 1991–1992 booklet of Threshold Limit Values(2) lists carbon tetrachloride with an A2 designation, which indicates chemical substances "associated with industrial processes, which are suspect of inducing cancer, based on either limited epidemiological evidence or demonstration of carcinogenesis in one or more animal species by appropriate methods."(2)

As a result of the toxicity of carbon tetrachloride, NIOSH instituted a program to find a suitable replacement substance for carbon tetrachloride in evaluating organic vapor (OV) and gas cartridges and canisters. Further, the Environmental Protection Agency recently proposed to conform its stratospheric ozone protection regulations (40 CFR, Part 82) to the requirements of Title VI of the Clean Air Act Amendments of 1990 (Public Law 101-549). This will result in the phasing-out of carbon tetrachloride production. Thus, it became essential to conduct the testing necessary to find an acceptable replacement test substance for carbon tetrachloride. This report presents data collected on OV cartridges designed for use on nonpowered, negative-pressure respirators.

Background

The current respirator certification regulations for chemical cartridges mandate testing in accordance with 30 CFR, Part 11,(3) Sections 11.162-8 and 11.183-7. Cartridges are tested "as received" from the applicant or after preconditioning at 25 or 85 percent relative humidity (RH). Varying flow rates and times are employed in the testing. A summary of the certification tests for OV and gas cartridges is given in Table 1. The rationale for equilibrating the cartridges at 25 or 85 percent RH, followed by testing at 50 percent RH and at a reduced flow rate, has been questioned.(4) It is thought that testing of as received cartridges over a broad range of RHs at the higher flow rate, 64 L/min, appears more indicative of use-type conditions.(4) Further, such testing might, in fact, constitute an improved and more realistic performance standard for testing OV and gas respirator cartridges. Truly, the fact that testing would be done under conditions more representative of use-type conditions is the most significant reason for justifying such a testing scheme.

The experimental work consisted of initial screening (phase one), followed by side-by-side testing against carbon tetrachloride (phase two). Four possible replacement agents (ethyl acetate, pentane, n-hexane, and heptane) were selected for screening based on their physical characteristics and toxicity, as well as reported charcoal adsorption characteristics.(5–8) Screening experiments tested cartridges as received from the manufacturer at 50 percent RH, 80 percent RH, and 25° ± 2°C with no preconditioning being performed. These tests were performed on a stacked-cartridge configuration which resembled a packed column or sorbent bed.(9) These tests were conducted at various challenge concentrations of carbon tetrachloride (control), ethyl acetate, pentane, n-hexane, and

TABLE 1. Summary of Organic Vapor Cartridge Certification Tests

Type of Respirator	Test Condition	Test Flow Rate (L/min)	Number of Tests	Minimum Life[A] (min)
Chemical cartridge organic vapor	As received	64	3	50
Chemical cartridge organic vapor	Equilibrated 25% RH	32	2	50
Chemical cartridge organic vapor	Equilibrated 85% RH	32	2	50
Powered air-purifying tight-fitting	As received	115[B]	3	50
Powered air-purifying tight-fitting	Equilibrated 25% RH	115[B]	2	25
Powered air-purifying tight-fitting	Equilibrated 85% RH	115[B]	2	25
Powered air-purifying loose-fitting hood or helmet	As received	170[B]	3	50
Powered air-purifying loose-fitting hood or helmet	Equilibrated 25% RH	170[B]	2	25
Powered air-purifying loose-fitting hood or helmet	Equilibrated 85% RH	170[B]	2	25

Test conditions are: 1000 ppm carbon tetrachloride and 50 percent RH; the minimum life is determined at 5 ppm breakthrough concentration.

[A] Cartridges designed for use against more than one type of agent; the minimum life shall be one-half of that shown above for each type of gas or vapor.

[B] Flow rate shall be the effective flow rate of the device, but not less than this flow rate.

heptane at 50 percent RH, 80 percent RH, and 25°C. (Warning: Ethyl acetate, pentane, n-hexane, and heptane are extremely flammable. Sparks and open flames must be avoided. Buildup of vapors in closed containers must also be avoided.) The purpose of the screening study was to identify potential replacement agents, challenge concentrations, and test conditions that would produce cartridge breakthrough times equivalent to the 1000 ppm carbon tetrachloride test.

The replacement agent(s)/challenge concentration conditions which showed equivalence with 1000 ppm carbon tetrachloride, based on breakthrough time as the critical evaluation criterion, were considered for further side-by-side testing against 1000 ppm carbon tetrachloride. This final side-by-side testing was to confirm that the test agent(s)/challenge concentration conditions gave cartridge breakthrough times equivalent to carbon tetrachloride at the most severe test condition. The side-by-side testing also determined which test condition was the most critical: equilibrated cartridges, as per 30 CFR, Part 11; or as received cartridges run at a higher test RH (80%). Finally, the side-by-side tests were to be run in accordance with the certification test procedure rather than the stacked-cartridge method used for the initial screening of the replacement test agents.

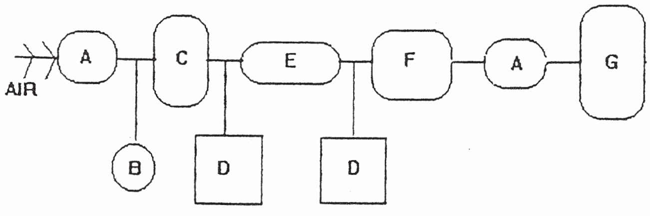
The breakthrough time data from the initial screening were used to select the agents for the side-by-side testing. The sole selection criterion was equivalency of breakthrough time with the 1000 ppm carbon tetrachloride 30 CFR, Part 11 certification test. However, other factors such as toxicity of the agent at the challenge concentration, water insolubility comparable to carbon tetrachloride, laboratory safety issues, and the existence of a suitable analytical detection system had to be considered.

The modified Wheeler equation was used for evaluating all the initial screening data.(9) The equation is as follows:

$$t_b = \frac{W_e}{C_o Q}\left[W - \frac{\rho_\beta Q}{k_\nu}\ln\left(C_o/C_x\right)\right] \tag{1}$$

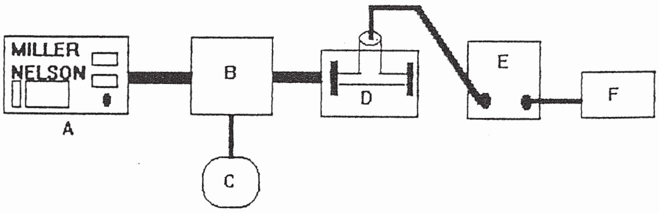
where:

t_b = breakthrough time (min)
C_x = exit concentration (g/cm^3)
C_o = inlet concentration (g/cm^3)
Q = volumetric flow rate (cm^3/min)
W = weight of adsorbent (g)
ρ_β = bulk density of the packed bed (g/cm^3)
W_e = kinetic adsorption capacity or equilibrium adsorption capacity at an arbitrary ration of C_x/C_o (g/g)
k_ν = first-order rate constant of adsorption (per min)



A – FLOW CONTROL MECHANISM
B – VAPOR GENERATOR
C – BUFFER RESERVOIR TANK
D – MIRAN 1A GAS ANALYZER
E – CARTRIDGE CELL
F – SORBENT SCRUBBER
G – VACUUM SOURCE

FIGURE 1. Stacked-cartridge test system.



A. MILLER-NELSON RELATIVE HUMIDITY FLOW CONTROLLER
B. RESERVOIR
C. SYRINGE PUMP
D. CARTRIDGE CELL HOLDER
E. MIRAN 1A GAS ANALYZER
F. VACUUM PUMP

FIGURE 2. Carbon tetrachloride certification test system.

TABLE 2. Organic Vapor Cartridge Breakthrough Time (t_b) against 1000 ppm Carbon Tetrachloride for Stacked Cartridges of Manufacturer A at Equivalent of 64 L/min for Pair Configuration

% RH	Cumulative Charcoal Weight (Grams) Single Cartridge[A,B]	Calculated[C] Charcoal Weight (g) if in Pair Configuration	t_b Corrected to 1000 ppm (Minutes)		
			5 ppm	10 ppm	15 ppm
50	33.840	67.680	61.2	63.6	64.9
	66.137	132.274	156.0	158.1	159.2
	99.045	198.090	239.3	241.4	242.7
	131.121	262.242	333.4	335.7	336.0
50	33.334	66.668	64.4	67.4	68.5
	67.363	134.726	155.1	158.7	160.7
	100.622	201.244	249.6	253.9	258.4
	133.498	266.996	360.0	364.1	366.7
80	33.247	66.494	46.3	49.6	51.2
	67.738	135.476	110.3	113.5	115.0
	101.342	202.684	178.8	182.7	184.5
	136.443	272.886	246.7	250.7	253.0
80	33.236	66.472	51.3	52.9	54.5
	64.757	129.514	118.0	119.7	121.4
	97.027	194.054	190.0	192.1	193.8
	130.313	260.626	262.8	264.6	266.9

[A] Stacked single cartridges run at 32 L/min.
[B] Lot 1.
[C] Calculated = twice the single cartridge weight

The values for C_o, C_x, and Q are established by the experimental test conditions, as is the temperature that remains constant. The value of ρ_β—which is dependent on the fill weight, granular size, shape of the adsorbent, and fill volume—can be determined experimentally and is part of the manufacturer's production criteria.

Plots of breakthrough times (t_b) as a function of bed weight (W) gave a straight line where the slope and intercept allowed calculation of the kinetic adsorption capacity and the adsorption rate constant. The slope is equal to W_e/C_oQ, the y-axis intercept is equal to

$$\frac{-W_e\rho_\beta}{k_\nu C_o}\ln\frac{C_o}{C_x} \tag{2}$$

and the critical bed weight (W_c) is equal to ρ_β Q ln $(C_o/C_x)/k_\nu$. By knowing the slope, a value for W_e (kinetic adsorption capacity) can be determined. By inserting W_e into the y-axis intercept relationship, one can calculate the kinetic adsorption rate constant k_ν. Also, k_ν could be calculated from the x-axis intercept value.

The two test agent/challenge concentration systems which best satisfied the above criteria were selected for direct side-by-side carbon tetrachloride testing to compare the present 30 CFR, Part 11 test methods[3] with data generated on as received cartridges. The five test conditions were: (1) preconditioned 25 percent RH and tested at 50 percent RH and 32 L/min, (2) preconditioned at 85 percent RH and tested at 50 percent RH and 32 L/min, (3) as received tested at 25 percent RH and 64 L/min, (4) as received tested at 50 percent RH and 64 L/min, and (5) as received tested at 80 percent RH and 64 L/min. Conditions 1, 2, and 4 represent the present 30 CFR, Part 11 testing scheme, while conditions 3, 4, and 5 represent the testing scheme NIOSH is considering for future implementation.

Experimental Method

Phase one entailed the stacked-cartridge method for screening possible replacement agents and determining replacement challenge concentration. This technique, which monitors breakthrough time as a function of sorbent weight, was used because it is more discriminating than running single cartridges. Manufacturer A cartridges (pair configuration) were used, and the phase one stacked-cartridge experiments were performed at a test flow of 32 L/min.

Two different lots of cartridges were used for the initial screening, but only comparisons within a single lot were considered so as to eliminate lot-to-lot variation. The stacked-cartridge testing system is as shown in Figure 1. Dried air is passed through an in-line dryer/sorbent system to remove residual moisture and contaminants. The inlet air is controlled to regulate the temperature, humidity, and flow rate. This flow

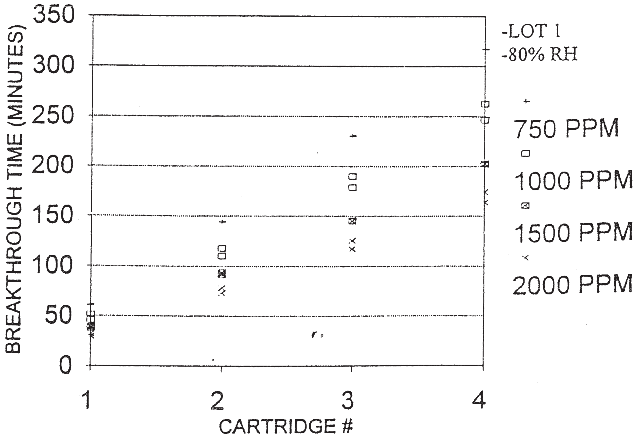


FIGURE 3. Carbon tetrachloride breakthrough data.

TABLE 3. Wheeler Constants for Manufacturer A Cartridges Against Carbon Tetrachloride at 5 ppm Breakthrough

				Slope					Intercept			Cartridge Wheeler Constants	
Lot	Challenge Concentration (ppm)	% RH	No. of Points	R^2	Slope	T	Pr>/T/	Y-Axis Intercept	T	Pr>/T/	W_e Kinetic Adsorption Capacity (g/g)	K_v Rate Constant ($-min^{-1}$)	W_c Critical Bed Weight (g)
1	750	50	8	0.998	3.945	59.32	0.0001	−48.36	−7.74	0.0002	0.596	4768	12.3
2	750	50	3	0.999	2.526	37.30	0.0171	−46.61	−6.61	0.0956	0.381	4457	18.5
1	750	80	8	0.999	2.455	177.02	0.0001	−25.22	−19.08	0.0001	0.339	5286	11.2
2	750	80	3	0.999	1.917	40.92	0.0156	−26.65	−5.52	0.1140	0.289	5852	13.9
1	1000	50	8	0.996	2.859	39.89	0.0001	−35.23	−5.41	0.0017	0.576	4842	14.6
2	1000	50	10	0.975	1.944	17.67	0.0001	−41.35	−3.04	0.0161	0.391	4080	25.3
1	1000	80	8	0.985	2.051	19.61	0.0001	−19.70	−2.07	0.0838	0.413	6281	9.6
2	1000	80	12	0.987	1.515	27.96	0.0001	−27.98	−3.94	0.0028	0.305	4666	18.5
1	1500	50	10	0.995	1.975	40.55	0.0001	−21.93	−5.22	0.0008	0.596	5932	11.1
2	1500	50	8	0.990	1.158	24.87	0.0001	−22.52	−3.72	0.0099	0.350	4761	19.5
1	1500	80	8	0.995	1.581	36.00	0.0001	−17.15	−4.12	0.0062	0.477	6181	10.9
2	1500	80	7	0.999	0.941	168.30	0.0001	−16.16	−23.97	0.0001	0.284	5434	17.2
1	2000	50	8	0.998	1.420	51.72	0.0001	−19.06	−7.14	0.0004	0.572	5402	13.4
1	2000	80	8	0.995	1.330	35.35	0.0001	−16.17	−4.52	0.0040	0.535	5819	12.2

rate can be varied up to 190 L/min, but must always exceed the flow rate pulled by the downstream vacuum source (G). This ensures that there is always positive overflow from the buffer reservoir to prevent atmospheric air from entering the system. The challenge concentrations for these experiments were generated and controlled using a syringe pump or Laboratory Data Control Minipump® (Riviera, Florida) to feed solvent to the airstream at a predetermined rate. By adjusting the pump feed rate and the inlet air flow rate, a known upstream concentration (C_o) could be established.

To reduce fluctuation in the upstream concentration, a buffer tank was added to the system. The upstream vapor concentration (C_o) and the downstream concentration (C_x) were continually monitored by means of a Miran 1A (Foxboro, Massachusetts) general-purpose infrared gas (IR) analyzer equipped with a variable path length gas cell. The analytical wavelength and minimum detectable limits, as specified by the manufacturer, with a 20-m cell for the test agents, were as follows: carbon tetrachloride, 12.6 μm and 1.1 ppm; ethyl acetate, 8.3 μm and 0.1 ppm; pentane, 3.4 μm and 0.2 ppm; n-hexane, 3.4 μm and 0.2 ppm; and heptane, 3.4 μm and 0.1 ppm.

The conditioned air stream (50 or 80 percent RH at 25°C) containing the challenge agent was then pulled through the cartridge cell housing which can contain from one to four cartridges in series. Another Miran 1A IR detector was located immediately downstream of the cartridges to monitor the breakthrough concentration as a function of exposure time. The exiting vapors were then passed through a sorbent scrubber before reaching the vacuum source.

The cell arrangement consisted of anodized aluminum pieces which had been machined to accept a specific commercially available OV respirator cartridge. The spacer units allowed for the stacking of one to four cartridges in series to resemble a packed column of varying bed length and sorbent weight, as well as containing sampling ports for the consecutive sampling of the gas downstream of each cartridge. Four breakthrough time versus breakthrough concentration measurements were obtained during a single experiment.

The data collection system operated similarly to the system previously described in the scientific literature.[9,10] The system was updated with a Hewlett-Packard (HP) series 200 computer in combination with an HP 3497A data acquisition system. In addition, all data were stored on a 3½-inch disk for future data analysis.

The phase two side-by-side testing was done per the present certification testing procedure with only minor modification. This test system is as shown in Figure 2. The testing conditions were the five noted earlier for conducting the side-by-side carbon tetrachloride testing comparison. Two different manufacturers' cartridges (B and C) were tested during the phase two side-by-side testing. Manufacturer B cartridges (single-

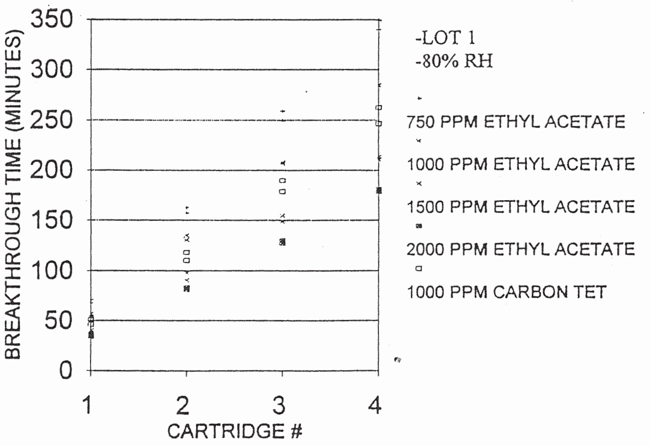


FIGURE 4. Carbon tetrachloride versus ethyl acetate breakthrough data.

TABLE 4. Wheeler Constants for Manufacturer A Cartridges Against Ethyl Acetate at 5 ppm Breakthrough

					Slope				Intercept			Cartridge Wheeler Constants	
Lot	Challenge Concentration (ppm)	% RH	No. of Points	R^2	Slope	T	Pr>/T/	Y-Axis Intercept	T	Pr>/T/	W_e Kinetic Adsorption Capacity (g/g)	K_v Rate Constant ($-min^{-1}$)	W_c Critical Bed Weight (g)
1	750	50	8	0.997	2.925	47.45	0.0001	−32.97	−5.43	0.0016	0.253	5438	11.3
1	750	80	8	0.994	2.528	31.08	0.0001	−22.14	−2.74	0.0338	0.219	7073	8.8
1	1000	50	8	0.999	2.356	77.74	0.0001	−28.69	−9.55	0.0001	0.272	5371	12.2
1	1000	80	8	0.998	2.083	57.24	0.0001	−20.02	−5.50	0.0015	0.240	6819	9.7
1	1500	50	8	0.998	1.774	55.71	0.0001	−22.53	−7.01	0.0004	0.307	5630	12.7
1	1500	80	8	0.999	1.584	63.79	0.0001	−20.39	−8.21	0.0002	0.274	5505	12.9
1	2000	50	4	0.999	1.342	46.61	0.0005	−13.25	−4.39	0.0482	0.310	8147	9.9
2	2000	50	4	0.995	1.211	19.90	0.0025	−23.50	−3.00	0.0953	0.279	4883	19.4
1 and 2	2000	50	8	0.958	1.211	11.72	0.0001	−12.19	−1.01	0.3534	0.279	8704	10.1
1	2000	80	8	0.999	1.319	82.16	0.0001	−13.37	−8.35	0.0002	0.304	7328	10.1

cartridge configuration) were of the OV type. Manufacturer C cartridges were of the OV type and organic vapor/acid gas (OV/AG) type cartridges (pair configuration). The major differences between the certification test system and the stacked-cartridge experiments were: (1) the air was pushed through the cartridges rather than being pulled through with a vacuum source, (2) a single or cartridge pair was mounted on a holder as employed on the respirator rather than stacking single cartridges in series, (3) the challenge concentration was determined gravimetrically (time-weighted average) rather than instantaneously over the entire test, (4) the breakthrough time was only determined at 5 ppm, and (5) a Teflon® needle resting on heated glass beads was employed when generating pentane.

The test agents evaluated were as follows: (1) carbon tetrachloride, Fisher Scientific, Pittsburgh, Pennsylvania, certified American Chemical Society (ACS) spectranalyzed, or Aldrich Chemical Company, Milwaukee, Wisconsin, ACS reagent 99 percent; (2) ethyl acetate, Fisher Scientific, certified ACS spectranalyzed; (3) n-pentane, Fisher Scientific, high pressure liquid chromatography (HPLC) grade; (4) n-heptane, Fisher Scientific, HPLC grade; and (5) n-hexane, either Fisher Scientific, certified ACS 99 mol% pure, or J.T. Baker Chemical Company, Phillipsburg, New Jersey, HPLC 97 percent. House air which was passed through a dryer/sorbent system to remove contaminants was used.

Results and Discussion

Breakthrough data for manufacturer A's cartridges against carbon tetrachloride for lot 1 and lot 2 serve as baseline data. Comparisons with other test agents were made within the same lot of cartridges, since it has been reported(11) that significant lot-to-lot variability can occur. Lot 1 data at 50 and 80 percent RH for stacked-cartridge experiments against a carbon tetrachloride challenge concentration of 1000 ppm are given in Table 2. Similar data for lot 1 stacked cartridges against carbon tetrachloride challenges of 750, 1500, and 2000 ppm were obtained, and Figure 3 is a plot of the 80 percent RH data. Similar data were collected for lot 2 cartridges at challenge concentrations of 750, 1000, and 1500 ppm of carbon tetrachloride at 50 and 80 percent RH. The Wheeler constants(9) which were calculated for both lots of cartridges at the various carbon tetrachloride challenge concentrations are presented in Table 3. These data represent the baseline data against which other compounds are compared.

Lot 1 cartridges were used in the testing of ethyl acetate. The breakthrough data for the stacked-cartridge phase one screening experiments at 50 and 80 percent RH against ethyl acetate concentrations of 750, 1000, 1500, and 2000 ppm were obtained. A typical graph of breakthrough time versus sorbent weight for the various ethyl acetate challenge concentrations is shown in Figure 4 (80% RH). Figure 4 also contains the 1000 ppm carbon tetrachloride baseline data for comparison. The Wheeler constant calculations at the various ethyl acetate challenge concentrations are presented in Table 4. These data show that the 1000 ppm ethyl acetate data are similar to the baseline 1000 ppm carbon tetrachloride data. But the main objection to the potential use of ethyl acetate is its water solubility, which

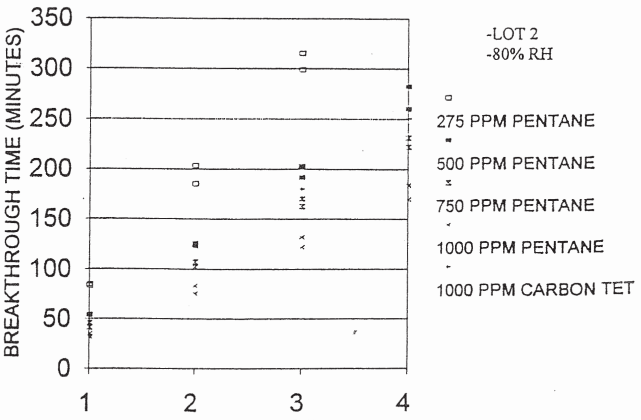


FIGURE 5. Carbon tetrachloride versus pentane breakthrough data.

TABLE 5. Wheeler Constants for Manufacturer A Cartridges Against Pentane at 5 ppm Breakthrough

						Slope			Intercept			Cartridge Wheeler Constants	
Lot	Challenge Concentration (ppm)	% RH	No. of Points	R^2	Slope	T	Pr>/T/	Y-Axis Intercept	T	Pr>/T/	W_e Kinetic Adsorption Capacity (g/g)	K_v Rate Constant ($-\text{min}^{-1}$)	W_c Critical Bed Weight (g)
2	275	50	6	0.958	3.746	9.55	0.0007	−40.36	−1.03	0.3594	0.097	5836	10.8
2	275	80	6	0.991	2.408	21.33	0.0001	−28.99	−2.55	0.0631	0.063	5271	12.0
2	500	50	8	0.996	2.445	39.01	0.0001	−34.52	−4.32	0.0050	0.116	5171	14.1
2	500	80	8	0.992	1.549	27.04	0.0001	−19.08	−2.60	0.0406	0.073	5850	12.3
2	750	50	8	0.989	1.746	22.98	0.0001	−31.05	−3.24	0.0178	0.124	4398	17.8
2	750	80	8	0.997	1.323	45.31	0.0001	−18.18	−4.89	0.0027	0.094	5316	13.7
2	1000	50	8	0.999	1.396	81.21	0.0001	−22.34	−10.22	0.0001	0.132	5234	16.0
2	1000	80	8	0.995	1.030	35.04	0.0001	−15.16	−4.06	0.0067	0.097	5697	14.7

introduces another variable, solubility of ethyl acetate in water occupying the micropores of the carbon structure.

The next agent investigated was pentane. Breakthrough stacked-cartridge data were obtained at 275, 500, 750, and 1000 ppm challenge concentrations for cartridge lot 2. The 80 percent RH data are plotted in Figure 5, and the Wheeler constants are given in Table 5. The 1000 ppm carbon tetrachloride data are included in Figure 5 for comparison, and show that the pentane breakthrough time data at 500 ppm are the closest to the carbon tetrachloride baseline curve.

Data for n-hexane were obtained for the stacked-cartridge configuration at challenge concentrations of 500, 750, 1000, and 1500 ppm. The breakthrough time versus sorbent weight data were employed in calculating the Wheeler constants, and are presented in Table 6. These data indicate that the n-hexane 1000 ppm data compare with the 1000 ppm carbon tetrachloride data and therefore n-hexane is a possible replacement agent.

The final agent tested was heptane. Heptane data were collected at 800, 1000, 1250, and 1500 ppm with the stacked cartridges. Table 7 presents the Wheeler constants calculated from the breakthrough time versus sorbent weight data. The data indicate that a challenge concentration of at least 1250 ppm is needed to give breakthrough times of the same order, as seen with 1000 ppm carbon tetrachloride. Based on these data and safety considerations, heptane was not deemed a suitable replacement agent.

The screening data identified potential replacement agents and challenge concentrations for additional testing. The evaluation was based solely on the equivalency of breakthrough time as compared with the 1000 ppm carbon tetrachloride control. The two best replacement candidates (pentane and n-hexane) were selected for direct comparison with carbon tetrachloride at the five conditions stated earlier in this report. These conditions represent the 30 CFR, Part 11 testing scheme with additional testing of as received cartridges at 25 and 80 percent RH (64 L/min). The first testing condition was pentane at 550 ppm, and the second was n-hexane at 1000 ppm. The results for manufacturer B OV cartridges and manufacturer C OV and OV/AG cartridges against 1000 ppm carbon tetrachloride (control), 550 ppm pentane, and 1000 ppm n-hexane are given in Table 8.

Table 8 reveals some interesting observations. First, the most stringent 30 CFR, Part 11 test condition (i.e., that which gave the shortest breakthrough time) for the OV cartridges was as received cartridges tested at 50 percent RH and 64 L/min. Second, the OV/AG cartridges' most stringent 30 CFR, Part

TABLE 6. Wheeler Constants for Manufacturer A Cartridges Against n-Hexane at 5 ppm Breakthrough

						Slope			Intercept			Cartridge Wheeler Constants	
Lot	Challenge Concentration (ppm)	% RH	No. of Points	R^2	Slope	T	Pr>/T/	Y-Axis Intercept	T	Pr>/T/	W_e Kinetic Adsorption Capacity (g/g)	K_v Rate Constant ($-\text{min}^{-1}$)	W_c Critical Bed Weight (g)
2	500	50	3	0.999	3.234	122.56	0.0052	−45.09	−16.74	0.0380	0.182	5311	14.0
2	500	80	3	0.999	2.328	43.94	0.0145	−30.18	−5.48	0.1149	0.131	5811	13.0
2	750	50	8	0.993	2.435	28.49	0.0001	−37.32	−3.42	0.0142	0.206	5188	15.3
2	750	80	7	0.999	1.827	59.91	0.0001	−22.19	−6.29	0.0015	0.155	6505	12.1
2	1000	50	8	0.999	1.786	66.46	0.0001	−22.00	−6.50	0.0006	0.202	6729	12.3
2	1000	80	8	0.999	1.528	78.95	0.0001	−24.73	−10.21	0.0001	0.172	5098	16.2
2	1500	50	8	0.999	1.427	79.51	0.0001	−24.25	−10.60	0.0001	0.242	5320	17.0
2	1500	80	8	0.999	1.260	129.09	0.0001	−18.47	−14.82	0.0001	0.213	6149	14.7

TABLE 7. Wheeler Constants for Manufacturer A Cartridges Against Heptane at 5 ppm Breakthrough

					Slope				Intercept			Cartridge Wheeler Constants	
Lot	Challenge Concentration (ppm)	% RH	No. of Points	R^2	Slope	T	Pr>/T/	Y-Axis Intercept	T	Pr>/T/	W_e Kinetic Adsorption Capacity (g/g)	K_v Rate Constant ($-min^{-1}$)	W_c Critical Bed Weight (g)
2	800	50	6	0.982	2.587	14.82	0.0001	−30.89	−1.78	0.1505	0.271	6693	11.9
2	800	80	6	0.981	2.394	14.30	0.0001	−35.29	−2.07	0.1067	0.251	5513	14.7
2	1000	50	8	0.981	2.100	17.70	0.0001	−33.63	−2.22	0.0685	0.275	5260	16.0
2	1000	80	8	0.997	1.974	46.79	0.0001	−32.08	−5.90	0.0011	0.259	5219	16.3
2	1250	50	8	0.989	1.815	22.75	0.0001	−29.09	−2.85	0.0293	0.298	5490	16.0
2	1250	80	8	0.998	1.700	56.51	0.0001	−32.46	−8.38	0.0002	0.279	4628	19.1
2	1500	50	8	0.996	1.629	37.87	0.0001	−31.63	−5.77	0.0012	0.320	4652	19.4
2	1500	80	6	0.974	1.129	12.25	0.0003	−16.55	−1.79	0.1483	0.222	6150	14.7

11 test condition was 85 percent RH preconditioned tested at 32 L/min and 50 percent RH. Third, all cartridges, even the OV/AG, had breakthrough times in excess of 50 minutes at all five test conditions. Fourth, the breakthrough times for the OV and OV/AG cartridges were of the same magnitude. Fifth, of all the tests performed, the most severe test condition was as received cartridges tested at 80 percent RH and 64 L/min.

The breakthrough times for manufacturer B and manufacturer C OV cartridges as received and tested at 64 L/min and 80 percent RH against 1000 ppm carbon tetrachloride were 68.6 and 76.6 minutes, respectively. The breakthrough times for manufacturer B and manufacturer C OV cartridges against 550 ppm pentane at the same test conditions (64 L/min and 80% RH) were 68.8 and 76.1 minutes, respectively. The breakthrough times for these OV cartridges against 1000 ppm n-hexane were 70.6 and 73.2 minutes. This indicates that 550 ppm pentane and 1000 ppm n-hexane should be suitable replacement agents for 1000 ppm carbon tetrachloride based on breakthrough times. However, correlation studies needed to be conducted to confirm these findings. Further, since it was shown that the most severe test condition was as received cartridges tested at 64 L/min and 80 percent RH, a strong case can be made to switch to a testing regimen that employs only as received cartridges and tests them at realistic use-type conditions (25, 50, and 80% RH).

Conclusions

The data show that, based on breakthrough time as the critical criterion, numerous test agents could be used instead of carbon tetrachloride for testing organic vapor cartridges. In fact, side-by-side testing of 1000 ppm carbon tetrachloride, 550 ppm pentane, and 1000 ppm n-hexane gave equivalent breakthrough times at the most severe test condition, which was as received cartridges tested at 80 percent RH and 64 L/min. But since pentane is considerably less toxic than n-hexane (600 and 50 ppm OSHA permissible exposure limits, respectively), pentane is the test agent of choice. Further, since the present 30 CFR, Part 11 equilibration tests are less discriminating than testing as received cartridges at use-type conditions, the test regimen should test as received cartridges at 25, 50, and 80 percent RH with a flow rate of 64 L/min.

TABLE 8. Cartridge Breakthrough Time Comparison Summary

	Breakthrough Time t_b (Minutes) Against 1000 ppm Carbon Tetrachloride			Breakthrough Time t_b (Minutes) Against 1000 ppm *n*-Hexane			Breakthrough Time t_b (Minutes) Against 550 ppm Pentane		
Conditions	Mfg B OV	Mfg C OV/AG	Mfg C OV	Mfg B OV	Mfg C OV/AG	Mfg C OV	Mfg B OV	Mfg C OV/AG	Mfg C OV
Preconditioned 25% RH test: 32 L/min 50% RH	219.6	201.9	210.5	178.9	178.7	191.6	222.0	217.9	232.3
Preconditioned 85% RH test: 32 L/min 50% RH	106.3	80.3	118.3	119.8	83.8	126.6	128.6	87.7	175.2
As received test: 64 L/min 25% RH	106.3	101.3	104.7	87.1	86.7	86.2	120.7	111.1	115.1
As received test: 64 L/min 50% RH	100.9	89.6	97.7	89.8	81.1	84.7	110.6	99.2	110.5
As received test: 64 L/min 80% RH	68.6	68.2	76.6	70.6	70.6	73.2	68.8	63.1	76.1

References

1. National Institute for Occupational Safety and Health: Occupational Health Guidelines for Chemical Hazards. DHHS (NIOSH) Pub. No. 81-123. NIOSH, Cincinnati, OH (1981).
2. American Conference of Governmental Industrial Hygienists: Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices for 1991–1992. ACGIH, Cincinnati, OH (1991).
3. Code of Federal Regulations Title 30, Part 11. 30 Mineral Resources, pp. 7–70. U.S. Government Printing Office, Office of the Federal Register, Washington, DC (1980).
4. Moyer, E.S.: Review of Influential Factors Affecting the Performance of Organic Vapor Air-Purifying Respirator Cartridges. Am. Ind. Hyg. Assoc. J. 44(1):46–51 (1983).
5. Nelson, G.O.; Harden, C.A.: Respirator Cartridge Efficiency Studies: V. Effects of Solvent Vapor. Am. Ind. Hyg. Assoc. J. 35:391–410 (1974).
6. Freedman, R.W.; Ferber, B.I.: Hartstein, A.M.: Service Lives of Respirator Cartridges Versus Several Classes of Organic Vapors. Am. Ind. Hyg. Assoc. J. 34(2):55–60 (1973).
7. Smoot, D.M.; Smith, D.L.: Development of Improved Respirator Cartridge and Canister Test Methods. NIOSH Report 77-209; NTIS Pub. No. PB 274-756. National Technical Information Service, Springfield, VA (1977).
8. Faust, C.L.; Herman, E.R.: The Adsorption of Alipathic Acetate Vapors onto Activated Carbon. Am. Ind. Hyg. Assoc. J. 30(5): 494–499 (1969).
9. Moyer, E.S.: Organic Vapor (OV) Respirator Cartridge Testing—Potential Jonas Model Applicability. Am. Ind. Hyg. Assoc. J. 48(9):791–797 (1987).
10. Wood, G.O.; Moyer, E.S.: A Review of the Wheeler Equation and Comparison of Its Application to Organic Vapor Respirator Cartridge Breakthrough Data. Am. Ind. Hyg. Assoc. J. 50(8): 400–407 (1989).
11. Trout, D.; Breysse, P.N.; Hall, T.; et al.: Determination of Organic Vapor Respirator Cartridge Variability in Terms of Degree of Activation of the Carbon and Cartridge Packing Density. Am. Ind. Hyg. Assoc. J. 47(8):491–496 (1986).

資料 13-b

Evaluation of Carbon Tetrachloride Replacement Agents for Use in Testing Nonpowered Organic Vapor Chin-Style Canisters

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For years, charcoal's ability to adsorb organic compounds has been evaluated employing carbon tetrachloride. The breakthrough characteristics for chin-style canisters against organic vapors mandate the use of carbon tetrachloride as per 30 CFR, Part 11. However, due to carbon tetrachloride's toxicity and the lack of commercial availability, a substitute organic vapor test agent is needed. This article deals with the evaluation of four potential substitute agents (ethyl acetate, pentane, n-hexane, and heptane) for testing chin-style canisters. Screening tests identified replacement agent challenge concentrations that gave breakthrough characteristics similar to 5000 parts per million (ppm) carbon tetrachloride. Side-by-side correlation testing was done between 4000 ppm pentane at 64 L/min, 80 percent relative humidity (RH), and 25°C with the most critical 30 CFR, Part 11 test condition (85% precondition followed by testing at 50% RH, 32 L/min, and 25°C). Finally, a reproducibility study was performed employing the 4000 ppm pentane system. The data show that pentane at 4000 ppm, 80 percent RH, 64 L/min, and 25°C correlated with carbon tetrachloride data, and that the pentane system gives reproducibility test breakthrough times. A pentane testing regimen using "as received" canisters tested at 25, 50, and 80 percent RH at a flow rate of 64 L/min and 25°C can be established to replace the present 30 CFR, Part 11 carbon tetrachloride test criteria for chin-style canisters.

MOYER, E.S.; PETERSON, J.A.; CALVERT, C.: EVALUATION OF CARBON TETRACHLORIDE REPLACEMENT AGENTS FOR USE IN TESTING NONPOWERED ORGANIC VAPOR CHIN-STYLE CANISTERS. APPL. OCCUP. ENVIRON. HYG. 10(9):769–775; 1995.

The National Institute for Occupational Safety and Health has instituted a program to find a suitable replacement substance for carbon tetrachloride in evaluating organic vapor (OV) and gas cartridges and canisters. This program was expeditiously conducted, since carbon tetrachloride is a suspected carcinogen,(1,2) and is in limited supply. The Environmental Protection Agency recently proposed to conform its stratospheric ozone protection regulations (40 CFR 82) to the requirements of Title VI of the Clean Air Act Amendments of 1990 (PL 101-549). This action has affected the supplies of carbon tetrachloride, immediately limiting the supply and perhaps ultimately causing it to be phased out of production. The Code of Federal Regulations (30 CFR, Part 11) mandates carbon tetrachloride for testing organic vapor and gas cartridges and canisters. Therefore, it is necessary to find a suitable substitute test agent to replace carbon tetrachloride.

Moyer *et al.*(3) have reported on nonpowered negative pressure OV cartridge breakthrough characteristics against four potential replacement agents (ethyl acetate, pentane, n-hexane, and heptane). This evaluation identified replacement agent challenge concentrations that gave breakthrough characteristics equivalent to 1000 parts per million (ppm) carbon tetrachloride. Breakthrough time was the sole critical criterion. Two test conditions (550 ppm pentane and 1000 ppm n-hexane) were selected for side-by-side testing with 1000 ppm carbon tetrachloride. The results show that for the most critical test condition ["as received" cartridges tested at 64 L/min and 80% relative humidity (RH)] the breakthrough times for two different manufacturers' organic vapor cartridges were identical for these three test conditions (1000 ppm carbon tetrachloride, 550 ppm pentane, and 1000 ppm n-hexane). Due to pentane's lower toxicity, it was recommended as the replacement agent of choice.

This article presents breakthrough time data obtained for chin-style canisters against the four potential replacement agents studied previously for OV nonpowered negative pressure cartridges. The major difference in the testing conditions was that higher challenge concentrations were employed because chin-style canisters contain 2.5 to 3.0 times more sorbent than cartridges. The regulations (30 CFR, Part 11)(4) require a carbon tetrachloride challenge concentration of 5000 ppm to be used when testing chin-style canisters.

Background

Chin-style canisters are presently tested and certified under 30 CFR, Part 11,(4) Subparts I and M. The specific performance requirements are given in 11.102-1 through 11.102-5 and 11.183-1 through 11.183-7. OV chin-style canisters are tested against a carbon tetrachloride challenge concentration of 5000 ppm. The specific test requirements are summarized in Table 1. Chin-style canisters are tested as received from the applicant and after preconditioning at either 25 or 85 percent RH. Varying flow rates are employed, but the minimum service life is 12 minutes at the various test conditions.

The rationale for equilibrating the canisters at 25 and 85 percent RH, followed by testing at 50 percent RH and at a

TABLE 1. 30 CFR, Part 11 Organic Vapor Tests for Chin-Style Canisters Against 5000 ppm Carbon Tetrachloride Challenge

Test Condition	Test Flow Rate (L/min)	No. of Tests	Maximum Allowable Penetration (ppm)	Minimum Service Life (min)
As received	64	3	5	12
Equilibrated 25% RH	32	2	5	12
Equilibrated 85% RH	32	2	5	12

All tests run at 50 percent RH.

TABLE 2. Summary of Chin-Style Canister Breakthrough Time Data Against Various Carbon Tetrachloride Challenge Concentrations

Challenge Concentration (ppm)	Charcoal Weight (g)	% RH	Breakthrough Time Corrected to Challenge Concentration (min) 5 ppm	10 ppm	15 ppm
1000	201.8	50	140.2	146.5	150.5
1000	208.4	80	121.7	127.0	131.0
2000	194.2	50	69.7	73.5	75.3
2000	193.3	80	61.1	64.5	66.2
5000	200.4	50	36.8	38.4	39.2
5000	204.6	80	33.1	34.8	35.6
10,000	203.9	50	21.3	22.4	22.6
10,000	201.8	80	18.1	19.2	19.9

Lot A canister.

reduced flow rate, has been questioned.(5) Further, it is thought that testing of as received canisters over a broad range of RHs at the higher flow rate, 64 L/min, appears more indicative of use-type conditions.(6) Such testing might, in fact, constitute an improved and more realistic performance standard for evaluating OV and gas respirator canisters.

Four possible replacement agents (ethyl acetate, pentane, n-hexane, and heptane) were selected and screened based on their physical characteristics and toxicity, as well as reported charcoal adsorption characteristics.(6–9) Chin-style canisters were tested as received from the manufacturer at 50 percent RH, 80 percent RH, and 25° ± 2°C with no preconditioning being performed. These tests were conducted at various challenge concentrations of carbon tetrachloride (control), ethyl acetate, pentane, n-hexane, and heptane at 50 percent RH, 80 percent RH, and 25°C. (Warning: ethyl acetate, pentane, n-hexane, and heptane are extremely flammable, and sparks and open flames must be avoided. Buildup of fumes in closed containers must be avoided. Further, the lower flammability limits for these agents are as follows: ethyl acetate, 22,000 ppm; pentane, 15,000 ppm; n-hexane, 11,000 ppm; and heptane, 10,500 ppm.) This portion of the study was to identify which potential replacement agent(s) at what challenge concentration would give chin-style canister breakthrough times equivalent to the 5000 ppm carbon tetrachloride test presently mandated in 30 CFR, Part 11.

The replacement agent(s)/challenge concentration conditions that showed equivalence with 5000 ppm carbon tetrachloride, based on breakthrough time as the critical evaluation criterion, were considered for further side-by-side correlation testing against 5000 ppm carbon tetrachloride. The correlation testing was to confirm that the test agent(s)/challenge concentration conditions gave cartridge breakthrough times equivalent to carbon tetrachloride at the most severe test condition. Further, the correlation testing determined which test condition was the most critical: equilibrated canisters, as per 30 CFR, Part 11; or as received canisters run at a higher test RH (80% RH).

Finally, a study was conducted to evaluate the reproducibility of the experimental testing procedure.

Experimental Method

The test configuration for the initial tests on single canisters is as shown in Figure 1 and has been described previously.(9) Individual chin-style canisters were tested as received from the manufacturer at a flow rate of 64 L/min through the canister. The test humidities were 50 and 80 percent, and the temperature was 25° ± 1.5°C. Various challenge concentrations of carbon tetrachloride (control) and potential replacement agents (ethyl acetate, pentane, n-hexane, and heptane) were tested. Breakthrough times were determined as the single critical

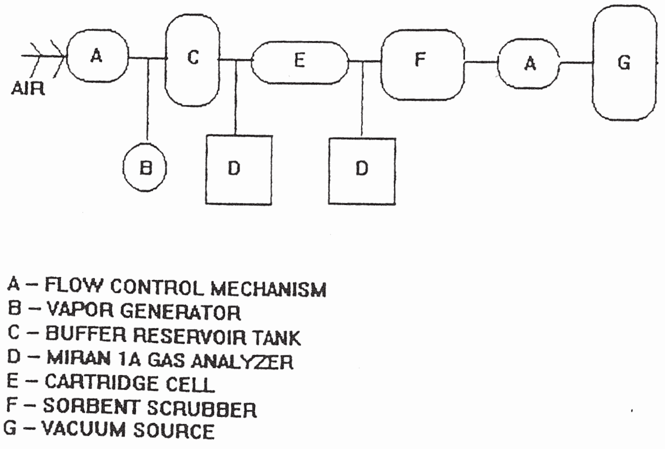

FIGURE 1. Canister test system.

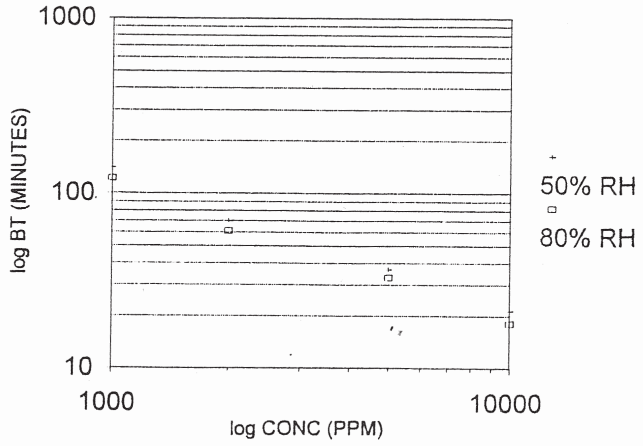

FIGURE 2. Carbon tetrachloride breakthrough data.

TABLE 3. Summary of Chin-Style Canister Breakthrough Time Data Against Various Ethyl Acetate Challenge Concentrations

Challenge Concentration (ppm)	Lot	Charcoal Weight (g)	% RH	Breakthrough Time Corrected to Challenge Concentration (min)		
				5 ppm	10 ppm	15 ppm
1000	C	201.5	50	127.4	132.0	134.7
1000	C	198.5	50	125.4	129.9	132.8
1000	A	192.0	80	78.0	81.5	83.8
1000	C	190.3	80	97.7	108.6	113.6
1000	C	199.4	80	98.8	107.4	110.8
2000	A	186.4	50	55.7	57.6	59.5
2000	A	184.2	80	44.0	46.2	48.0
5000	B	182.0	50	24.5	25.4	26.2
5000	B	182.5	80	16.6	17.3	17.9
7500	C	201.4	50	20.1	21.1	21.6
7500	B	202.7	80	10.8	17.4	18.1

criterion for determining equivalency with carbon tetrachloride.

Subsequent side-by-side testing was done as per the certification testing procedure with minor modification. These tests directly compared the replacement agent with the control carbon tetrachloride at 50 and 80 percent RH on as received canisters at 25°C. One manufacturer's chin-style canister was tested. The major experimental differences between the certification test system and the one shown in Figure 1 are (1) the air is pushed through the chin-style canisters rather than being pulled with a vacuum source, (2) a single canister is mounted on a holder as employed on the respirator, (3) the challenge concentration is determined gravimetrically rather than instantaneously over the entire test, (4) the breakthrough time is only determined at 5 ppm, and (5) the Teflon® needle rested on heated glass beads in the case of pentane. These equipment differences should not have any effect on the data obtained.

The detector system was a Miran 1A (Foxboro) general purpose infrared gas analyzer equipped with a variable path length gas cell. The analytical wavelength and minimum detectable limits, as specified by the manufacturer, with a 20-m cell for the test agents, are as follows: carbon tetrachloride, 12.6 μm and 1.1 ppm; ethyl acetate, 8.3 μm and 0.1 ppm; pentane, 3.4 μm and 0.2 ppm; n-hexane, 3.4 μm and 0.2 ppm; and heptane, 3.4 μm and 0.1 ppm.

TABLE 4. Summary of Chin-Style Canister Breakthrough Time Data Against Various Pentane Challenge Concentrations

Challenge Concentration (ppm)	Charcoal Weight (g)	% RH	Breakthrough Time Corrected to Challenge Concentration (min)		
			5 ppm	10 ppm	15 ppm
1000	205.9	50	78.6	80.9	82.7
1000	207.9	80	73.8	76.9	79.0
2000	203.0	50	56.7	58.5	59.8
2000	214.7	80	49.8	51.7	53.0
5000	203.7	50	32.9	34.2	34.9
5000	216.7	80	30.4	32.3	33.0
7500	213.7	50	23.3	24.2	24.8
7500	218.5	80	21.1	22.1	23.1

Lot C canister.

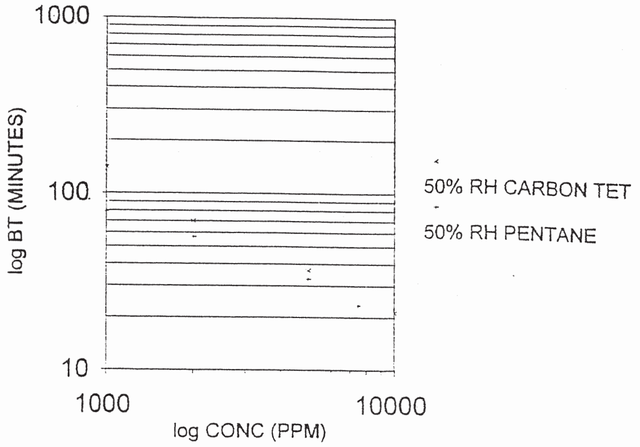

FIGURE 3. Carbon tetrachloride versus pentane. Breakthrough data at 50 percent RH.

The test agents evaluated were as follows: (1) carbon tetrachloride, Fisher Scientific, Pittsburgh, Pennsylvania, certified American Chemical Society (ACS) spectranalyzed, or Aldrich Chemical Company, Milwaukee, Wisconsin, ACS reagent 99 percent; (2) ethyl acetate, Fisher Scientific, certified ACS spectranalyzed; (3) n-pentane, Fisher Scientific, high pressure liquid chromatography (HPLC) grade; (4) n-heptane, Fisher Scientific, certified ACS 99 mol% pure, or J.T. Baker Chemical Company, Phillipsburg, New Jersey, HPLC 97 percent. House air which was passed through a dryer/sorbent system to remove contaminants was used.

Results and Discussion

The breakthrough data for the chin-style canisters against carbon tetrachloride are presented in Table 2. Challenge concentrations of 1000, 2000, 5000, and 10,000 ppm were used.

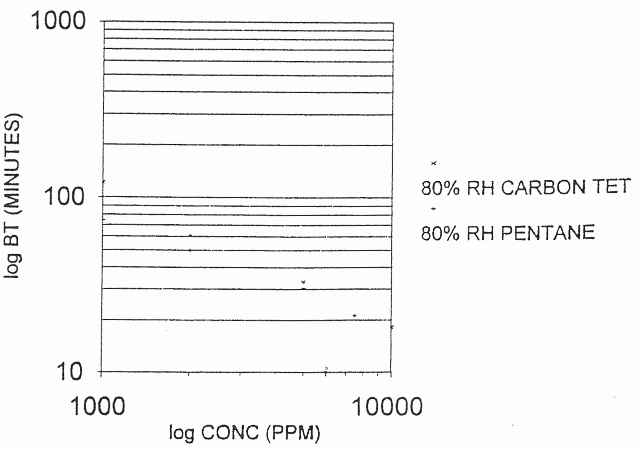

FIGURE 4. Carbon tetrachloride versus pentane. Breakthrough data at 80 percent RH.

TABLE 5. Summary of Chin-Style Canister Breakthrough Time Data Against Various *n*-Hexane Challenge Concentrations

Challenge Concentration (ppm)	Charcoal Weight (g)	% RH	Breakthrough Time Corrected to Challenge Concentration (min) 5 ppm	10 ppm	15 ppm
1000	208.5	50	106.0	109.7	111.9
1000	200.5	80	97.2	101.7	103.5
2000	209.8	50	55.4	57.2	58.5
2000	210.6	80	53.7	55.8	57.3
5000	202.3	50	28.7	30.0	30.6
5000	202.5	80	32.7	34.0	34.6
7000	199.8	50	21.2	22.2	22.7
7000	200.9	80	21.4	22.6	23.5

Lot C canister.

TABLE 6. Summary of Chin-Style Canister Breakthrough Time Data Against Various Heptane Challenge Concentrations

Challenge Concentration (ppm)	Charcoal Weight (g)	% RH	Breakthrough Time Corrected to Challenge Concentration (min) 5 ppm	10 ppm	15 ppm
2500	200.8	50	59.2	61.7	63.3
2500	202.2	80	57.1	59.5	61.6
5000	198.8	50	25.9	27.3	27.9
5000	206.6	80	26.0	27.7	28.6
7500	202.1	50	19.0	20.4	21.0
7500	202.5	80	15.5	17.4	18.2

Lot C canister.

Tests were conducted at 50 and 80 percent RH. A plot of the data presented in Table 2 is shown in Figure 2. At higher challenge concentrations, the resulting increase in the challenge concentration to water ratio reduces the competitive effect of the water vapor. This was not the case with cartridges that were run at a lower concentration (1000 ppm) and where the sorbent weight for cartridges was significantly lower than for chin-style canisters (130 to 250 g).

The chin-style canister breakthrough data against ethyl acetate concentrations of 1000, 2000, 5000, and 7500 ppm at 50 and 80 percent RH are given in Table 3. Likewise, the breakthrough data against pentane concentrations of 1000, 2000, 5000, and 7500 ppm are presented in Table 4. Figures 3 and 4 illustrate the data comparison between carbon tetrachloride and pentane at 50 and 80 percent RH, respectively.

The n-hexane data at challenge concentrations of 1000, 2000, 5000, and 7000 ppm are presented in Table 5 for 50 and 80 percent RH. Table 6 presents the heptane breakthrough data (2500, 5000, and 7500 ppm challenge concentrations). Table 7 summarizes all the chin-style canister breakthrough data at a 5 ppm penetration value.

Ethyl acetate was eliminated from further consideration as the replacement agent due to its water solubility, which could introduce another potential variable. The above data on pentane, n-hexane, and heptane were evaluated to identify the best agent and challenge concentration for further testing. The evaluation was based solely on the equivalency of breakthrough time as compared with the breakthrough time of the 5000 ppm carbon tetrachloride control. The best candidate for direct comparison with 5000 ppm carbon tetrachloride was determined to be 4000 ppm pentane.

As received chin-style canisters underwent additional testing at 50 and 80 percent RH (64 L/min) employing the certification test methodology. The results for the 5000 ppm carbon tetrachloride (control) and 4000 ppm pentane are given in Table 8. These data confirm previous results that indicate there is little difference in breakthrough times between the 50 and 80 percent RH conditions at these higher challenge concentrations and added sorbent weights.

The breakthrough times for the chin-style canisters against 5000 ppm carbon tetrachloride were 39.6 and 35.7 minutes at 50 percent RH as compared with 38.1 and 37.5 minutes against 4000 ppm pentane. The 80 percent RH breakthrough times against 5000 ppm carbon tetrachloride were 38.5 and 35.1 minutes as compared with 36.3 and 40.7 minutes against 4000 ppm pentane. These data indicate that 4000 ppm pentane

TABLE 7. Summary of Chin-Style Canister Breakthrough Data at 5 ppm Penetration

Challenge Agent	Test RH (%)	Breakthrough Time at Challenge Concentration (min) 1000 ppm	2000 ppm	2500 ppm	5000 ppm	7000 ppm	7500 ppm	10,000 ppm
Carbon tetrachloride	50	140.2	69.7		36.8			21.3
	80	121.7	61.1		33.1			18.1
Ethyl acetate	50	127.4	55.7		24.5		20.1	
	50	125.4						
	80	78.0	44.0		16.6		10.8	
	80	97.7						
	80	98.8						
Pentane	50	78.6	56.7		32.9		23.3	
	80	73.8	49.8		30.4		5 21.1	
n-Hexane	50	106.0	55.4		28.7	21.2		
	80							
Heptane	50			59.2	25.9		19.0	
	80			57.1	26.0		15.5	

TABLE 8. Comparison of Breakthrough Times Against 4000 ppm Pentane and 5000 ppm Carbon Tetrachloride for As Received Manufacturer A Organic Vapor Chin-Style Canisters

	Test RH (%)	Weight of Canisters (g)					Breakthrough Time at 5 ppm (min)
		Initial	Final	ΔW	Case	Sorbent	
Pentane	50	415.0	441.0	26.0	211.6	203.4	38.1
Pentane	50	409.0	435.1	26.1	211.0	198.0	37.5
Carbon tetrachloride	50	410.8	473.5	62.7	212.2	198.6	39.6
Carbon tetrachloride	50	409.0	468.0	59.0	211.6	197.4	35.7
Pentane	80	413.9	443.2	29.3	213.2	200.7	36.3
Pentane	80	410.1	439.1	29.0	210.8	199.3	40.7
Carbon tetrachloride	80	410.0	479.0	69.0	214.0	196.0	38.5
Carbon tetrachloride	80	417.8	468.9	51.1	211.7	206.1	35.1

All tests run at 64 L/min.

TABLE 9. Organic Vapor Cartridge Breakthrough Time Correlation Data for Chin-Style Canisters

			5000 ppm CCL_4, 64 L/min, 50% RH, 25°C		5000 ppm CCL_4, 85% Preconditioned, 32 L/min, 50% RH, 25°C		4000 ppm Pentane, 64 L/min, 80% RH, 25°C	
Manufacturer	Lot	Run	Sorbent Weight (g)	Breakthrough Time at 5 ppm (min)	Sorbent Weight (g)	Breakthrough Time at 5 ppm (min)	Sorbent Weight (g)	Breakthrough Time at 5 ppm (min)
A	A	1	249.5	52.1	232.6	48.8	243.3	51.3
		2	237.2	56.9	236.0	38.0	245.3	51.0
B	A	1	200.0	42.4	198.1	17.8	203.7	37.2
		2	200.3	34.5	204.7	28.9	204.9	37.3
C	A	1	134.3	46.4	134.5	42.5	154.0	44.8
		2	135.7	44.8	149.5	41.4	154.5	43.7

TABLE 10. Breakthrough Time Reproducibility Study Against 4000 ppm Pentane for Manufacturer B Organic Vapor Chin-Style Canisters at 50 Percent RH and 64 L/min

Sample Number	Weight of Cartridges (g)					Breakthrough Time at 5 ppm (min)
	Initial	Final	ΔW	Case	Sorbent	
1	407.5	433.2	25.7	211.8	195.7	36.1
2	409.2	436.1	26.9	212.6	196.6	38.1
3	415.5	442.0	26.5	212.6	202.9	37.2
4	414.9	441.0	26.1	213.2	201.7	36.0
5	415.0	442.0	27.0	213.1	201.9	38.6
6	413.2	439.1	25.9	211.8	201.4	37.3
7	415.5	441.9	26.4	213.2	202.3	38.3
8	415.0	441.0	26.0	212.7	202.3	40.3
9	416.5	442.0	25.5	210.6	205.9	37.3
10	415.0	440.8	25.8	214.1	200.9	39.3

TABLE 11. Breakthrough Time Reproducibility Study Against 4000 ppm Pentane for Manufacturer B Organic Vapor Chin-Style Canisters at 80 Percent RH and 64 L/min

Sample Number	Weight of Cartridges (g)					Breakthrough Time at 5 ppm (min)
	Initial	Final	ΔW	Case	Sorbent	
1	412.9	441.5	28.6	211.7	201.2	36.4
2	418.2	448.0	29.8	210.8	207.4	35.7
3	413.1	442.1	29.0	212.3	200.8	36.7
4	412.1	439.1	27.0	213.3	198.8	36.0
5	409.6	440.9	31.3	211.7	197.9	33.8
6	405.0	433.0	28.0	212.2	192.8	34.6
7	409.9	439.5	29.6	213.1	196.8	41.0
8	416.6	446.0	29.4	213.2	203.4	34.8
9	408.0	437.9	29.9	210.8	197.2	37.6
10	408.9	436.9	28.0	213.6	195.3	32.7

appears to be a suitable replacement agent for 5000 ppm carbon tetrachloride based on breakthrough times. Further, all chin-style canisters had breakthrough times substantially longer than the 12 minutes required in 30 CFR, Part 11.

Next, a correlation study was done employing the two best candidates. Direct comparison with carbon tetrachloride controls was determined. The data for three manufacturers' chin-style cartridges are presented in Table 9. Data for the carbon tetrachloride controls at two certification conditions (as received and preconditioned at 85% RH) are compared with the as received test data at 80 percent RH for pentane (4000 ppm) and n-hexane (5000 ppm).

The correlation data in Table 9 indicate that in the case of chin-style canisters, the most critical 30 CFR, Part 11 test condition for the OV canister was the 85 percent preconditioned canisters tested at 5000 ppm, 32 L/min, 50 percent RH, and 25°C. This is not consistent with the cartridge data which identified the most critical test to be on as received cartridges tested at 1000 ppm, 50 percent RH, and 64 L/min. Also, the canister data showed little difference in breakthrough times between the 50 and 80 percent RH test conditions for as received canisters with either pentane or carbon tetrachloride. Significant differences were observed at these conditions for the cartridges. These differences are due to the higher challenge concentration for canisters (5000 ppm) as compared to cartridges (1000 ppm) and the increased canister sorbent weight (two to three times that of cartridges).

The chin-style canister correlation data in Table 9 compare the carbon tetrachloride 5000 ppm data with the pentane 4000 ppm data. A simple linear regression analysis comparison was done between these data. For the carbon tetrachloride (5000 ppm, 64 L/min, 50% RH, and 25°C) versus pentane (4000 ppm, 64 L/min, 80% RH, and 25°C) the equation of the line obtained was $y = 1.1492 \times -4.6323$ with an r^2 value of 0.8461. The equation of the correlation between the carbon tetrachloride (5000 ppm, 85% RH preconditioned, 32 L/min, 50% RH test, 25°C) versus pentane (4000 ppm, 64 L/min, 80% RH, and 25°C) was $y = 1.4548 \times -28.0947$ with an r^2 value of 0.6612. This shows that the preconditioned carbon tetrachloride data are more variable, resulting in a reduced r^2 value. The calculated point estimate for the pentane with the present most critical 30 CFR, Part 11 test (preconditioned at 85% RH) was found to be 27 minutes using the simple model. This model was used, since at present the number of manufacturers' products to evaluate is very limited. All manufactured products were evaluated as part of this study, and each product was tested in duplicate.

Finally, a set of experiments was conducted to determine the reproducibility of the pentane test procedure. The experiment was done employing the pentane 4000 ppm challenge concentration at both 50 and 80 percent RH on as received canisters. Tables 10 and 11 present the data for canisters of manufacturer B at 50 and 80 percent RH, respectively. The data at 50 percent RH gave a mean breakthrough time of 37.9 minutes with a standard deviation of 1.4, while the mean was 35.9 with a standard deviation of 2.3 for the 80 percent RH condition. These data agree with previous data and show that the breakthrough times at 50 and 80 percent RH are not significantly different. Further, the pentane procedure shows excellent reproducibility.

Conclusions

The data show that, based on breakthrough time as the critical criterion, 4000 ppm pentane is a suitable replacement for 5000 ppm carbon tetrachloride for testing organic vapor chin-style canisters. Side-by-side testing results showed the following: (1) that the breakthrough times for as received canisters tested at 50 and 80 percent RH and 64 L/min at 25°C gave quite similar breakthrough characteristics; (2) that the most severe 30 CFR, Part 11 test for chin-style canisters was 85 percent RH preconditioned canisters tested at 50 percent RH, 32 L/min, 25°C, and 5000 ppm carbon tetrachloride; (3) that correlation existed between the 4000 ppm pentane data and the 5000 ppm carbon tetrachloride data; and (4) that the point estimate between the 4000 ppm pentane (64 L/min, 80% RH, as received, and 25°C) and the most critical 30 CFR, Part 11 test (preconditioned at 85% RH and tested at 32 L/min, 50% RH, and 25°C) was 27 minutes using a regression model.

Pentane was the agent chosen to replace carbon tetrachloride for cartridge testing. Since pentane was found to be a suitable replacement agent for testing cartridges, it is logical to select pentane for chin-style canister testing. Also, pentane is the least toxic of the possible replacement agents studied. Finally, all breakthrough times greatly exceeded the 12-minute criterion in 30 CFR, Part 11, even when testing as received canisters at 64 L/min. Thus, a testing regimen using only as received canisters at 25, 50, and 80 percent RH (25°C) at a flow rate of 64 L/min could be established.

References

1. National Institute for Occupational Safety and Health: Occupational Health Guidelines for Chemical Hazards. DHHS (NIOSH) Pub. No. 81-123. NIOSH, Cincinnati, OH (1981).
2. American Conference of Governmental Industrial Hygienists: Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices for 1991–1992. ACGIH, Cincinnati, OH (1991).
3. Moyer, E.S.; Peterson, J.A.; Calvert, C.: Evaluation of Carbon Tetrachloride Replacement Agents For Use in Testing Nonpowered Organic Vapor Cartridges. Appl. Occup. Environ. Hyg. 10(9):000–000 (1995).
4. Code of Federal Regulations Title 30, Part 11. 30 Mineral Resources, pp. 7–70. U.S. Government Printing Office, Office of the Federal Register, Washington, DC (1980).
5. Moyer, E.S.: Review of Influential Factors Affecting the Performance of Organic Vapor Air-Purifying Respirator Cartridges. Am. Ind. Hyg. Assoc. J. 44(1):46–51 (1983).
6. Nelson, G.O.; Harder, C.A.: Respirator Cartridge Efficiency Studies: V. Effects of Solvent Vapor. Am. Ind. Hyg. Assoc. J. 35:391–410 (1974).
7. Freedman, R.W.; Ferber, B.I.; Hartstein, A.M.: Service Lives of Respirator Cartridges Versus Several Classes of Organic Vapors. Am. Ind. Hyg. Assoc. J. 34(2):55–60 (1973).
8. Smoot, D.M.; Smith, D.L.: Development of Improved Respirator Cartridge and Canister Test Methods. NIOSH Report 77-209; NTIS Pub. No. PB 274-756. National Technical Information Service, Springfield, VA (1977).
9. Faust, C.L.; Herman, E.R.: The Adsorption of Aliphatic Acetate Vapors onto Activated Carbon. Am. Ind. Hyg. Assoc. J. 30(5): 494–499 (1969).

資料 14(a)

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September 27, 1993

Letter to All Respirator Manufacturers
Subject: Carbon Tetrachloride Substitute Test Agent
for Nonpowered Negative-Pressure Organic Vapor Cartridges

The Environmental Protection Agency recently proposed conforming its stratospheric ozone protection regulations (40 CFR 82) to the requirements of Title VI of the Clean Air Act Amendments of 1990 (PL 101-549). This action has affected the supplies of carbon tetrachloride by immediately limiting and perhaps ultimately causing it to be phased out of production.

The Code of Federal Regulations (30 CFR Part 11, Subpart L, Section 11.162-8) mandates the use of carbon tetrachloride for testing organic vapor cartridges. Therefore, it has become necessary to find a suitable substitute test agent. The National Institute for Occupational Safety and Health (NIOSH) has conducted research to this end. Testing of substitute agents, at various challenge concentrations and testing conditions, identified certain agents with breakthrough characteristics similar to carbon tetrachloride.

Testing has shown that the single most critical nonpowered negative pressure cartridge test condition, under the requirements of 30 CFR 11.162.8, is the "as received" condition, with testing performed at 1000 ppm, 64 LPM, 50% relative humidity (RH), 25 degrees C and a 50-minute minimum breakthrough time. The preconditioning requirements were not addressed because they have been shown to be less critical, time consuming, variable, and not representative of use-type RH conditions.

Correlation testing, performed to match the "as received" parameters, resulted in pentane at 550 ppm, 64 LPM, 80% RH, 25°C, and a 40 minute breakthrough time. The threshold point estimate for pentane was determined using a parametric survival model assuming that the failure times of the cartridges follow a Weibull distribution.

Therefore, the Certification and Quality Assurance Branch will now accept the use of pentane in place of carbon tetrachloride for all certification and quality control work. Note, however, that pentane is highly volatile. Proper cautions and information, such as material safety data sheets, should be observed.

Substitution is not limited to pentane. Other agents may be used. However, data demonstrating equivalency of the selected agent with carbon tetrachloride must be provided by the respirator manufacturer.

For the present, NIOSH will continue using carbon tetrachloride as the test agent and will change to pentane when carbon tetrachloride is no longer readily available.

If we can be of any further assistance, please contact Dr. Ernest S. Moyer, Ph.D. at (304) 284-5714.

Sincerely yours,

Richard W. Metzler

Richard W. Metzler, Chief
Certification and Quality
Assurance Branch
Division of Safety Research

資料 14(b)

DEPARTMENT OF HEALTH & HUMAN SERVICES Public Health Service

Centers for Disease Contr
National Institute for Oc
Safety and Health — ALC
944 Chestnut Ridge Roa
Morgantown, WV 26505

December 29, 1993

Letter to All Respirator Manufacturers
Subject: Carbon Tetrachloride Substitute Test Agent
for Nonpowered Negative-Pressure Organic Vapor
Chin-Style Canisters

The Environmental Protection Agency recently proposed conforming its stratospheric ozone protection regulations [Title 40, Code of Federal Regulations, Part 82 (40 CFR 82)] to the requirements of Title VI of the Clean Air Act Amendments of 1990 (PL 101-549). This action has affected the supplies of carbon tetrachloride by immediately limiting and perhaps ultimately causing it to be phased out of production.

Title 30, Code of Federal Regulations, Part 11, (30 CFR 11) Subpart L, Section 11.162-8, mandates the use of carbon tetrachloride for testing organic-vapor cartridges. Therefore, it has become necessary to find a suitable substitute test agent. The National Institute for Occupational Safety and Health (NIOSH) has conducted research to this end. Testing of substitute agents at various challenge concentrations and testing conditions identified certain agents with breakthrough characteristics similar to carbon tetrachloride.

Testing has shown that the most critical nonpowered negative-pressure, chin-style canister test condition under the requirements of 30 CFR 11.102-5 and 11.183-7 is the 85% relative humidity (RH) preconditioned canisters with carbon tetrachloride testing performed at 5000 ppm, 32 LPM, 50% RH, and 25°C at a minimum breakthrough time of 12 minutes at 5 ppm breakthrough concentration.

Correlation testing performed to match the 85% RH preconditioned canister parameters, resulted in testing canisters "as received" with pentane at 4000 ppm, 64 LPM, 80% RH, and 25°C. The maximum breakthrough is 5 ppm at a 27-minute breakthrough time. Thus, the new testing regimen would consist of "as received" chin-style canisters tested at 25%, 50%, and 80% RH, 4000 ppm pentane, 5 ppm breakthrough concentration, and a minimum breakthrough time of 27 minutes.

The Certification and Quality Assurance Branch will now accept the use of pentane in place of carbon tetrachloride for all certification and quality control work. Note, however, that pentane is highly volatile and flammable. Proper precautions should be exercised.

Substitution is not limited to pentane. Other agents may be used. However, data demonstrating equivalency of the selected agent with carbon tetrachloride must be provided by the respirator manufacturer.

For the present, NIOSH will continue using carbon tetrachloride as the test agent and will change to pentane when carbon tetrachloride is no longer readily available.

If we can be of any further assistance, please contact Dr. Ernest S. Moyer at (304) 284-5714.

Sincerely yours,

Don Campbell for

Richard W. Metzler, Chief
Certification and Quality
Assurance Branch
Division of Safety Research

資料 14(c)

DEPARTMENT OF HEALTH & HUMAN SERVICES

Public Health Service

Centers for Disease Control
and Prevention (CDC)
National Institute for Occupation
Safety and Health - ALOSH
944 Chestnut Ridge Road
Morgantown, WV 26505-2888

March 25, 1994

Letter to All Respirator Manufacturers

Subject: Carbon Tetrachloride Substitute Test Agent for Nonpowered Negative-Pressure Organic Vapor Front Mounted/Back Mounted Canisters

The Environmental Protection Agency recently proposed conforming its stratospheric ozone protection regulations [Title 40, Code of Federal Regulations (CFR), Part 82 (40 CFR 82)] to the requirements of Title VI of the Clean Air Act Amendments of 1990 (PL 101-549). This action has affected the supplies of carbon tetrachloride by immediately limiting, and perhaps ultimately causing it to be phased out of production.

Title 30, CFR Part 11 (30 CFR 11), Subpart L, Section 11.162-8, mandates the use of carbon tetrachloride for testing organic-vapor cartridges and canisters. The National Institute for Occupational Safety and Health (NIOSH) has conducted research to find a suitable substitute test agent. Testing of substitute agents at various challenge concentrations and testing conditions identified certain agents with breakthrough characteristics similar to carbon tetrachloride.

Testing has shown that the most critical nonpowered negative-pressure, chin-style canister test condition under the requirements of 30 CFR 11.102-5 and 11.183-7 is the 85% relative humidity (RH) preconditioned canisters with carbon tetrachloride testing performed at 5000 ppm, 32 LPM, 50% RH, and 25°C at a minimum breakthrough time of 12 minutes at 5 ppm breakthrough concentration. Correlation testing on "as received" chin-style canisters with pentane at 4000 ppm, 64 LPM, 80% RH, and 25°C showed that a 27-minute breakthrough time at 5 ppm correlated with the 30 CFR 11 test on 85% RH preconditioned canisters against carbon tetrachloride.

Nonpowered organic vapor front-mounted/back-mounted (FM/BM) canister's bench test conditions are contained in 30 CFR 11, Subpart I - Gas Masks (Table 5), and Subpart M - Pesticide Respirators (Table 12). Testing showed that the most critical nonpowered negative-pressure FM/BM canister test condition in 30 CFR 11 is the 85% RH preconditioned canisters with carbon tetrachloride testing performed at 20,000 ppm, 32 LPM, 50% RH, and 25°C with a minimum breakthrough time of 12 minutes at a 5 ppm breakthrough concentration.

Laboratory testing was performed to match the 85% RH preconditioned canister parameters. Since pentane was the replacement agent for cartridge and chin-style canisters, it was preselected for use with FM/BM canisters. Since pentane's lower explosive limit is 14,000 ppm, 10,000 ppm was the upper concentration limit studied for safety reasons. Results showed that "as received" canisters tested with pentane at 10,000 ppm, 64 LPM, 80% RH, and 25°C with a minimum breakthrough time of 50 minutes at a 5 ppm breakthrough concentration correlated with the most critical FM/BM canister test condition in 30 CFR 11. Thus, the new testing regimen would consist of "as received" FM/BM canisters being tested at 25%, 50%, and 80% RH, 10,000 ppm pentane, 5 ppm breakthrough concentration, and a minimum breakthrough time of 50 minutes.

The Certification and Quality Assurance Branch will now accept the use of pentane in place of carbon tetrachloride for all certification and quality control work. Note, however, that pentane is highly volatile and flammable. Proper precautions should be exercised.

Substitution is not limited to pentane. Other agents may be used. However, data demonstrating equivalency of the selected agent with carbon tetrachloride must be provided by the respirator manufacturer.

For the present, NIOSH will continue using carbon tetrachloride as the test agent and will change to pentane when carbon tetrachloride is no longer readily available.

If we can be of any further assistance, please contact Mr. William Hoffman at (304) 284-5713.

Sincerely yours,

Richard W. Metzler, Chief
Certification and Quality
Assurance Branch
Division of Safety Research

資料 14 (d)

DEPARTMENT OF HEALTH & HUMAN SERVICES

Public Health Service

Centers for Disease Control
and Prevention (CDC)
National Institute for Occupationa
Safety and Health - ALOSH
944 Chestnut Ridge Road
Morgantown, WV 26505-2888

July 28, 1994

Letter to All Respirator Manufacturers
Subject: Carbon Tetrachloride Substitute Test Agent for Powered Air Purifying Respirator (PAPR) Organic Vapor Cartridges

The Environmental Protection Agency recently proposed conforming its stratospheric ozone protection regulations [Title 40, Code of Federal Regulations (CFR), Part 82 (40 CFR 82)] to the requirements of Title VI of the Clean Air Act Amendments of 1990 (PL 101-549). This action has affected the supplies of carbon tetrachloride by immediately limiting, and perhaps ultimately causing it to be phased out of production.

The Code of Federal Regulations (30 CFR Part 11, Subpart L, Section 11.162-8, and Subpart M, Section 11.183-7) mandates the use of carbon tetrachloride for testing PAPR organic vapor cartridges. Therefore, it has become necessary to find a suitable substitute test agent. The National Institute for Occupational Safety and Health (NIOSH) has conducted research to this end. Testing of substitute agents, at various challenge concentrations and testing conditions, identified certain agents with breakthrough characteristics similar to carbon tetrachloride.

Testing has shown that the most severe PAPR organic vapor cartridge test condition under the requirements of 30 CFR 11.162-8 and 11.183-7 is the 85% relative humidity (RH) preconditioned cartridges with carbon tetrachloride testing performed at 1000 ppm, 50% RH, 25°C, and a flowrate of 115 lpm for tight-fitting facepieces or 170 lpm for loose-fitting hoods or helmets. The minimum breakthrough requirement is 25 minutes at a 5 ppm breakthrough concentration.

Laboratory testing has been conducted to match the 85% preconditioned cartridge results against carbon tetrachloride with pentane results on "as received" cartridges tested at 550 ppm, 80% RH, 25°C, and at a flowrate of 115 lpm for tight-fitting facepieces or 170 lpm for loose-fitting hoods or helmets. A breakthrough time of 50 minutes at a 5 ppm breakthrough concentration of pentane corresponded to the 85% preconditioned cartridge carbon tetrachloride data. The threshold point estimate for pentane was determined using a parametric survival model, assuming that the failure times of the cartridges follow a Weibull distribution.

The Certification and Quality Assurance Branch will now accept the use of pentane in place of carbon tetrachloride. The new testing regimen would consist of "as received" PAPR cartridges tested at 25%, 50%, and 80% RH, 550 ppm pentane, 5 ppm breakthrough concentration, and a minimum breakthrough time of 50 minutes.

Substitution is not limited to pentane. Other agents may be used. However, data demonstrating equivalency of the selected agent with carbon tetrachloride must be provided by the respirator manufacturer.

For the present, NIOSH will continue using carbon tetrachloride as the test agent and will change to pentane when carbon tetrachloride is no longer readily available.

If we can be of any further assistance, please contact Mr. William Hoffman at (304) 284-5713.

Sincerely yours,

Don Campbell for

Richard W. Metzler, Chief
Certification and Quality
Assurance Branch
Division of Safety Research

資料 15

Racal Filter Technologies, Ltd.

Comments on Conclusions from "Evaluation of Carbon Tetrachloride Replacement Agents for Testing Organic Vapor Cartridges".

Simon J. Smith Racal Filter Technologies Ltd. 11th April 1993

Racal greatly appreciates the detailed work that NIOSH has undertaken towards the goal of carbon tetrachloride replacement. The generation of such an in-depth study over a short time has been a great service to the industry.

Racal fully support these efforts, and the Research and Development Department at Racal Filter Technologies Ltd. (Brockville, Ontario, Canada) has undertaken work over recent months to generate additional data for comparison of powered air purifying respirator criteria.

The removal of the pre-humidification requirement and its replacement by increased/diminished test humidity is welcomed as providing a more realistic representation of most typical usage conditions.

It should incidentally be noted that carbon tetrachloride is the organic vapour test agent in the internationally adopted European standards EN141 (negative pressure) and prEN146 (powered air [under development]). To our knowledge, there is no unified effort under way in the European Community to choose a replacement, although the same time constraints for carbon tetrachloride elimination apply. The conclusions of the replacement study by NIOSH will doubtless be of interest beyond the United States.

There are some observations on the conclusions of this report that Racal would like to make.

Commentary

The NIOSH study concluded with generation of comparative data for carbon tetrachloride, hexane and pentane under "equivalent" test conditions. There was no significant difference between the performance of hexane and pentane as replacement test agents for cartridge tests at appropriate concentrations. NIOSH concluded that pentane should be the agent of choice on the grounds of lower toxicity. Racal has experience in the use of a wide range of organic test agents, and notes difficulties with pentane. We would therefore like to present some observations on the test data and to present further information on practical problems.

3. In plots at both relative humidities, data for all organics *except* pentane lie close to the carbon tetrachloride line.
4. Hexane generally has the closest equivalence to carbon tetrachloride for both relative humidities.
5. (Incidental): the lines for ethyl acetate are not far removed from carbon tetrachloride in both cases in spite of the water solubility of the former. Solubility may possibly not be a problem if NIOSH is pursuing non-pre-humidified tests as the standard procedure.

C. Toxicity

NIOSH cites toxicity as a reason for choosing pentane over hexane as cartridge test data are otherwise equivalent at the concentrations chosen. Racal believes toxicity not to be a significant consideration in this case:

1 Any laboratory currently undertaking testing with carbon tetrachloride is working with a toxic carcinogen and environmental hazard, and equipment design and procedures reflect this. Presumably, substitution of any less toxic material should be no problem.

2. There would therefore be no concern with the use of any less toxic material in a replacement protocol. In this case, the greater toxic hazard - hexane - is an order of magnitude less toxic than carbon tetrachloride.

3. Under these circumstances, the relative difference in toxicity between pentane and hexane is a side issue.

D. Conclusions

Hexane would appear to the best choice based on:

1. Ease of practical use compared with difficulties of pentane.
2. Closest equivalence of both break time-concentration and break time-bed size plots based on NIOSH data.
3. In a choice between pentane and hexane, toxicity is not an issue.

Racal supports the choice of hexane rather than pentane as the replacement agent for carbon tetrachloride.

RESULTS OF TESTS ON ORGANIC VAPOUR CARTRIDGES AT POWERED AIR FLOW RATES

General Test Conditions:

Flow Rate:	57 LPM	Temperature:	22-24°C
Humidity:	As Indicated	Break Concentration:	5 ppm

Vapour generation by evaporation of liquid.
Effluent concentration detection by infrared spectrophotometer.

1. Carbon Tetrachloride

Concentration	50 % R.H. Test		80 % R.H. Test	
	Break Times	Average	Break Times	Average
(ppm)	(min)	(min)	(min)	(min)
1,000	142,156,162	153	125,146,159	143
2,000	86,87,88	87	76,82,82	80
5,000	35,36,40	37	34,36,39	36
10,000	16,18,21	18	16,16,18	17
Log-Log Plot:				
Slope	-0.930		-0.918	
Intercept	98095		83721	

2. Ethyl Acetate

Concentration	50 % R.H. Test		80 % R.H. Test	
	Break Times	Average	Break Times	Average
(ppm)	(min)	(min)	(min)	(min)
1,000	163,167,168	166	143,148,153	148
2,000	81,81,87	83	58,70,89	72
5,000	33,37,38	36	28,28,33	30
10,000	15,16,18	16	14,14,16	15
Log-Log Plot:				
Slope	-0.995		-0.999	
Intercept	161647		145334	

Simon J. Smith
RACAL FILTER TECHNOLOGIES LTD.
Aug. 93.

RESULTS OF TESTS ON ORGANIC VAPOUR CARTRIDGES AT POWERED AIR FLOW RATES

General Test Conditions:

Flow Rate:	57 LPM	Temperature:	22-24°C
Humidity:	As Indicated	Break Concentration:	5 ppm

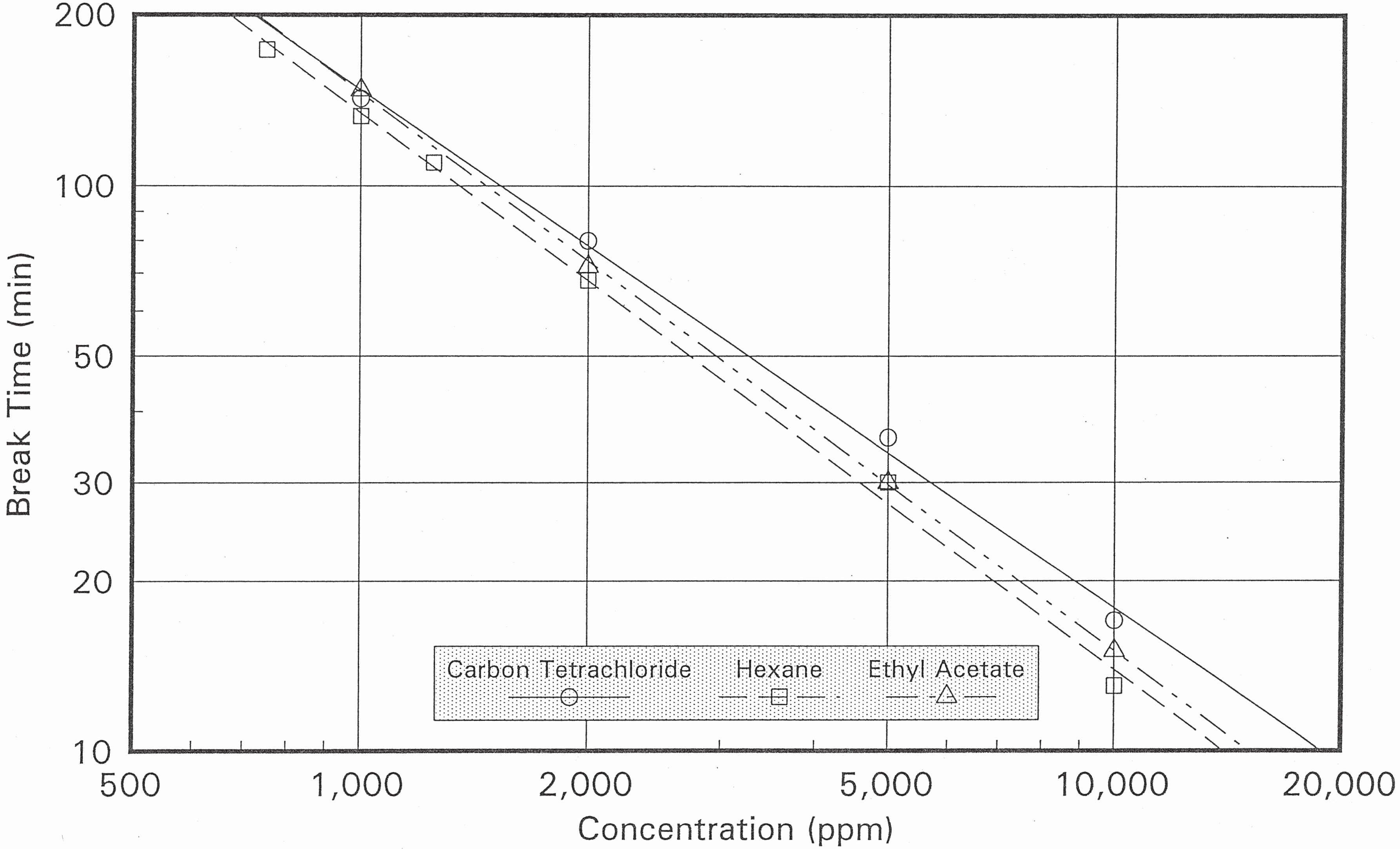
Vapour generation by evaporation of liquid.
Effluent concentration detection by infrared spectrophotometer.

Hexane

Concentration	50 % R.H. Test		80 % R.H. Test	
	Break Times	Average	Break Times	Average
(ppm)	(min)	(min)	(min)	(min)
750	170,174,174	173	153,175,193	174
1,000	126,134,147	136	125,136,138	133
1,250	114,116,117	116	105,115	110
2,000			67,68,70	68
5,000	28,29,30	29	29,30,30	30
10,000	15,17,17	16	11,12,16	13
Log-Log Plot:				
Slope	-0.931		-0.988	
Intercept	84500		124000	

Comparison of Standard Organic Vapour Test

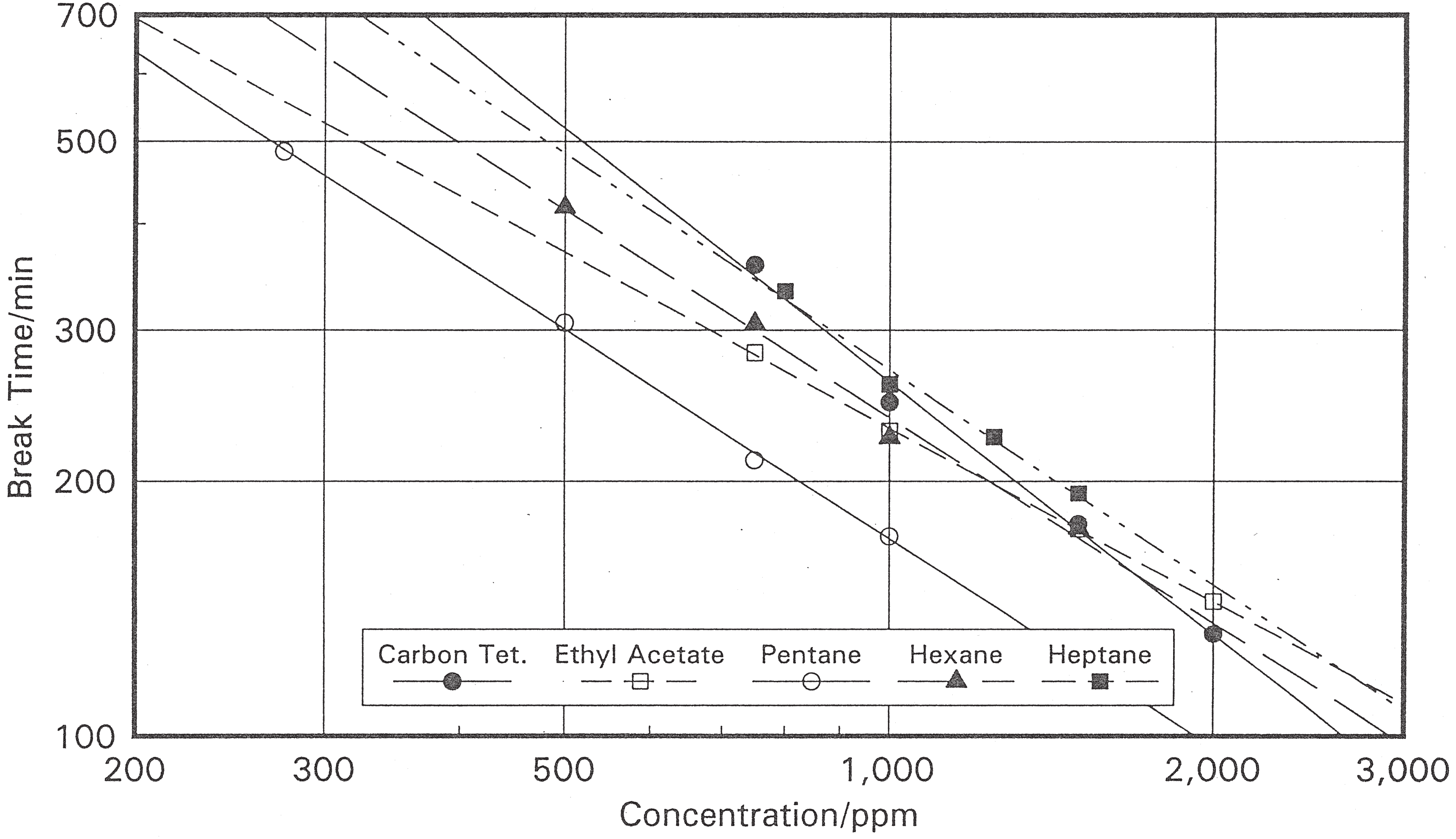
Type A Cartridges at 57 LPM, 80% RH, 5ppm Break



Canisters with 270 cc Coconutshell base carbon

COMPARISON OF BREAK TIME WITH CONCENTRATION

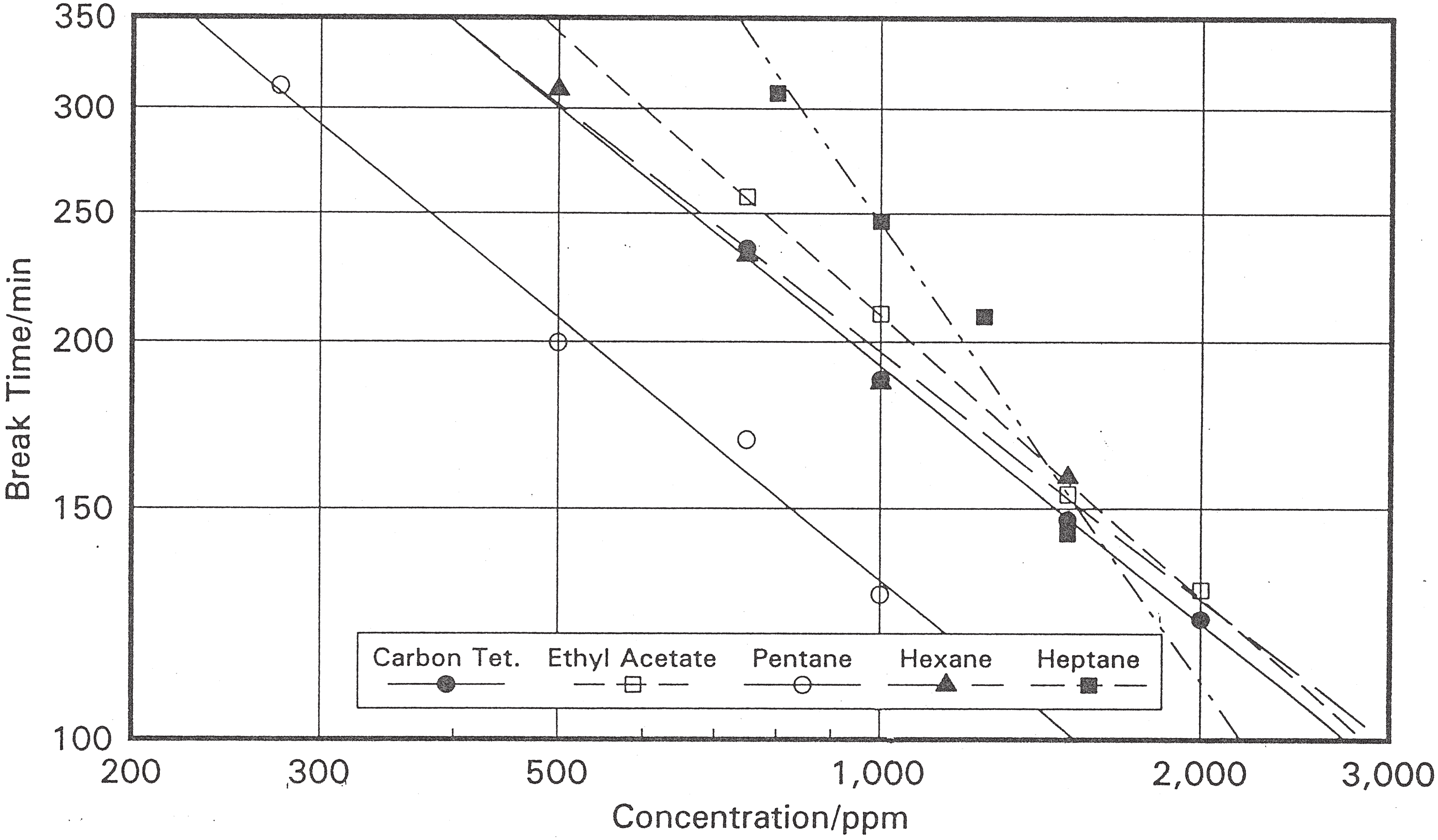
NIOSH DATA: 32 LPM AND 50% R.H.



Data from 3rd Cartridge, 10 ppm Break

COMPARISON OF BREAK TIME WITH CONCENTRATION

NIOSH DATA: 32 LPM AND 80% R.H.



Data from 3rd Cartridge, 10 ppm Break

Racal
Filter Technologies,
Ltd.

1175 California Ave.
P.O. Box 665
Brockville, Ontario
K6V 5V8
Tel: 613-345-0111
Fax: 613-345-2639

13th August 1993

Dr. Yoshimi Matsumura,
Department of Environmental Hygiene,
National Institute of Industrial Health,
21-1, Nagao 6 Chome,
Tama-ku,
Kawasaki-214,
Japan

Dear Dr. Matsumura,

Thank you very much for your comprehensive reply to my letter. This information is most useful. I have now received full confirmation that I shall be attending the ISRP Conference, so I look forward to meeting you there. I shall be staying in Japan for one week after the Conference also.

I have enclosed a report by Dr. Ernest Moyer, of the National Institute for Occupational Safety and Health (NIOSH) describing work undertaken there on carbon tetrachloride replacement. After testing a range of organic vapours, the conclusion is made that pentane makes the best replacement agent. NIOSH are basing their new approval requirements on this choice also, although this is not liked by a number of independent test agencies and manufacturers. In view of the concern, NIOSH have agreed to accept test results based on any organic compound, provided that correlation to pentane can be shown. Dr. Moyer has told me that he is planning to publish these results later this year. I have obtained his permission to send you this copy of the report, but he has asked that the data be treated confidentially at present.

I am also enclosing some data that we have determined here for tests with ethyl acetate and hexane in comparison with carbon tetrachloride. These were submitted to NIOSH, prior to their decision to use pentane. Note that the flow rates are non-standard - we use 57 litres per minute on one 270 cc canister - as they are used in threes on Racal powered air purifying respirators, which operate at 170 LPM. The data are in the form of logarithmic break time versus concentration plots, which we find the most useful for adsorbent, adsorbate and service life comparison. I have re-plotted certain data from the NIOSH report in this form also

資料17

TECHNICAL ADVANCES IN PERSONAL PROTECTION

Session 2

Alternatives To Carbon Tetrachloride For Canister Testing

by

Paul Malloy

THE ASSOCIATED OCTEL COMPANY LIMITED
PO BOX 17
OIL SITES ROAD
ELLESMERE PORT
SOUTH WIRRALL L65 4HS
UNITED KINGDOM

Tel: 051-355-3611 Fax: 051-356-2349

ABSTRACT

Due to increasing concern on health and environmental grounds regarding the use of carbon tetrachloride, CEN TC 79 SC4 decided that the use of this agent for testing gas filters should be discontinued as soon as possible.

When data from various sources on many potential alternative agents was examined, cyclohexane and 2 butanone emerged as front runners. An inter-laboratory trial of these two compounds was therefore instigated.

The reason for choosing these two compounds, the objectives of the trial and details of the programme of tests shall be discussed.

6542

OCTEL
ASSOCIATED OCTEL

Fax Message

To	Simon J Smith,	Fax No.	(613) 345-2639
Company	Racal Health & Safety, Ontario, CANADA.		
From	Safety Equipment Test Lab, HS&EA	File ref.	R.N.A.2.1.1
Date	25.10.94	Page 1 of	1 sheets
Copy to			

Dear Simon,

REPLACEMENT OF CTC AS TEST AGENT FOR EN141 TYPE A FILTERS

Cyclohexane has finally been accepted by Europe as the replacement for CTC. The decision was made at the CEN standards meeting at Chiswick (London) last week.

The following test protocol was also agreed:

Test agent: cyclohexane		
Filter type/class	Test concentration	Minimum time at test conditions
A1	0.1%	70 minutes
A2	0.5%	35 minutes
A3	0.8%	65 minutes

EN141 is due for revision next year and this amendment will be included.

Many thanks for your valued contributions, the data you provided, your involvement in the interlaboratory trial, etc. I hope the outcome meets with your approval.

Yours sincerely,

P. Malloy

Paul Malloy
Safety Equipment Test Laboratory,
Health, Safety & Environmental Affairs Dept.

H.S.& E.A. FAX NO. 051 356 6127

The Associated Octel Company Limited
PO Box 17, Oil Sites Road, Ellesmere Port, South Wirral L65 4HF Tel 051-355 3611 Fax 051-356 2349

資料 18

Sundstrom
Peltor
Stockhausen
Interspiro

Safety Equipment Australia Pty Ltd
A.C.N. 002 727 586
North Shore Business Park
35/1 Jubilee Avenue
Warriewood NSW 2102
Mail Priv Bag 1001, Mona Vale NSW 2103
Tel (02) 979 5077 Fax (02) 979 5364
SEA

April 21, 1995

Yoshimi Matsumura, Ph.D.
National Institute of Industrial Health
6-21-1 Nagao, Tama-ku
Kawasaki 214
Japan

Dear Yoshimi

I received your fax regarding Carbon Tetrachloride, and will get back to you shortly with some information. Currently Carbon Tetrachloride is being used as a test gas. Attached is a specification sheet on one of our filters - 315 (ABE 1)

It was a pleasure to hear from you and perhaps we may meet again at the upcoming I.S.R.P. Conference in Vancouver, Canada in September this year.

Regards

G Powe.

GRAHAM POWE
SALES MANAGER

North Region:
Suite 15, Garden Square
643 Kessels Road
Upper Mt Gravatt QLD 4122
PO Box 6219
Upper Mt Gravatt QLD 4122
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South Region:
38/1601 Malvern Road
Glen Iris VIC 3146
PO Box 3000
Glen Iris VIC 3146
Phone: (03) 823 4458
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West Region:
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550 Canning Highway
Alfred Cove WA 6154
Phone: (09) 317 3131
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South Australia:
1271 North East Road
Ridgehaven SA 5097
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St Agnes SA 5097
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Sundstrom
Peltor
Stockhausen
Interspiro

Safety Equipment Australia Pty Ltd
North Shore Business Park
35 Jubilee Avenue
Warriewood NSW 2102
Mail: Pty Bag 1001, Mona Vale NSW 2103
Tel: (02) 979 5077 Fax: (02) 979 5364
A.C.N. 002 727 586

SEA

Facsimile Cover Sheet

To: Mr Yoshimi Matsumura Ph.D.
Company: National Institute of Industrial Health
Phone:
Fax: 0011 81 44 865 6116

From: Goran Berndtsson
Company: Safety Equipment Australia Pty Ltd
Phone: (02) 979-5077
Fax: (02) 979-5364

Date: 26/4/95
Pages including this cover page: 1

Graham Powe has passed onto me your fax regarding Gas Mask Tests. The new American Standard and updated version of EN 141 will be looking on alternative gases but at this stage these have not been finalised.

Australia will follow whichever country is first to implement such a change.

Unfortunately this is all the information I can offer you at this stage. However, if I can be of any further assistance, please do not hesitate to contact me.

Regards,

Goran Berndtsson
per

orth Region:
uite 15, Garden Square
43 Kessels Road
pper Mt Gravatt QLD 4122
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