

# Cross-sensitivities of electrochemical detectors used to monitor worker exposures to airborne contaminants: False positive responses in the absence of target analytes

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Ideally, the response of electrochemical detectors is proportional to the concentration of targeted airborne chemicals and is not be affected by concomitantly present substances. Manufacturers provide a limited list of cross-sensitivities but end-users have anecdotally reported unexpected interferences by other substances. Electrochemical detectors designed to measure airborne levels of CO, H<sub>2</sub>S, NO, NO<sub>2</sub>, or SO<sub>2</sub>, were challenged with potentially interfering substances in the absence of target analytes. Cross-sensitivities undocumented by the manufacturers were observed and were found to vary between different models of instruments for the same challenge chemical.

## Introduction

Portable, lightweight electrochemical detectors are the most common type of personal, direct-reading instrument used to measure concentrations of toxic gases. The target chemicals diffuse through a porous membrane to the sensing electrode and the detector measures differences in chemical potential, the resulting signal being proportional to the concentration of the target chemicals present in air. Other substances having an oxidation-reduction (redox) potential equal to or less than the target chemical may increase or decrease this signal resulting in positive or negative interference (also known as cross-sensitivity, relative response or interference response).

Manufacturers of electrochemical detectors normally supply a limited list of cross-sensitivities known to affect a particular model of instrument. Cross sensitivities documented by manufacturers of various carbon monoxide (CO), hydrogen sulfide (H<sub>2</sub>S), nitric oxide (NO), nitrous oxide (NO<sub>2</sub>), or sulfur dioxide (SO<sub>2</sub>) detectors include: acetylene, carbon monoxide, chlorine, ethylene, hydrogen, hydrogen chloride, hydrogen cyanide, hydrogen sulfide, nitric oxide, nitrogen dioxide, sulfur dioxide, ethylene, hydrogen, nitric oxide, nitrous oxide, and hydrogen sulfide. Presentation of this information in the product literature is generally confusing and open to interpretation. There is little or no information concerning test conditions, and it is not specified whether or not the challenge gas was present alone or together with the instrument's target chemical.

Two previous studies found that Draeger's Datalogger 190 carbon monoxide detector gave false readings in the presence of ammonia, but the ammonia concentration was not specified.<sup>1,2</sup> It was found that the detector was unaffected by the presence of a mixture of 2.5% methane and 0.6% propane, or

by 18 ppm NO<sub>2</sub>, 9 ppm H<sub>2</sub>S, or 21 ppm SO<sub>2</sub>.<sup>3</sup> The authors did, however, find that it responded strongly to the presence of 40 ppm NO, 500 ppm H<sub>2</sub>, or 1% ethylene, giving readings of 77 ppm, 33 ppm and 200 ppm, respectively. Two studies evaluated H<sub>2</sub>S electrochemical detectors but they did not include the Biosystems, BW, or ISC instruments.<sup>4,5</sup> There is little or no other information to be found in the scientific literature concerning electrochemical detector cross-sensitivities.

Field technicians and industrial hygienists using direct-reading electrochemical detectors have anecdotally reported unexpected interferences by substances other than those documented by manufacturers, notably alcohols and solvents.<sup>6</sup> Examples where false positive readings were thought to occur included the following industries: printing where alcohols are used; plastics and printing where ketones are used; chemical factories where aliphatic and aromatic hydrocarbons are used; food factories where alcohol is used; pulp and paper plants and composting facilities where sulfur compounds are present; and in agricultural and waste management and establishments where ammonia, carbon dioxide, and nitrous oxide are found.

The objective of this study was to identify possible undocumented cross-sensitivities of amperometric electrochemical detectors commonly used to evaluate worker exposures to airborne contaminants. The aim is to provide occupational hygienists with information that will allow them to better select direct-reading instruments for a particular application or to modify their workplace evaluation strategy.

## Experimental

Instruments from four manufacturers of electrochemical detectors currently used by field technicians and hygienists from the Quebec public occupational health network were selected for this study. A total of 25 amperometric instruments designed to measure CO, H<sub>2</sub>S, NO, NO<sub>2</sub>, or SO<sub>2</sub> were tested in the absence of their respective target analytes: Toxilog (CO, H<sub>2</sub>S, NO<sub>2</sub>, SO<sub>2</sub>) and ToxiUltra (CO, H<sub>2</sub>S, NO, NO<sub>2</sub>) from

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**Table 1** Number of detectors tested

Target chemical	Biosystems Toxilog	Biosystems ToxiUltra	BW Gas Alert	Draeger Datalogger	ISC TX418
Carbon monoxide (CO)	2	2	1	2	2
Hydrogen sulfide (H <sub>2</sub> S)	1	1			2
Nitric oxide (NO)		2			
Nitrogen dioxide (NO <sub>2</sub> )	2	2	1		
Sulfur dioxide (SO <sub>2</sub> )	2		1		2

Biosystems Inc., BW GasAlert (CO, NO<sub>2</sub>, SO<sub>2</sub>) from BW Technologies Inc., ISC Model TX 418 (CO, H<sub>2</sub>S, SO<sub>2</sub>) from Industrial Scientific Corporation, and Datalogger 190 (CO) from Draeger Incorporated (Table 1). None of the instruments tested included internal chemical filters.<sup>7–11</sup> All detectors were calibrated with a certified gas. They were used according to manufacturers' instructions, and a stable zero baseline was obtained prior to each test. The challenge chemicals selected were potential interferents known to be present concomitantly with target substances measured in workplaces where electrochemical detectors are commonly used to assess worker exposures (Table 2).

In the case of solvents, instruments were exposed to challenge compounds in a hermetically sealed, 0.01 m<sup>3</sup> glass test chamber, built at the IRSST and placed inside a fumehood.<sup>12</sup> An experiment consisted of three successive 120 minute test challenges to a single compound or mixture with the ambient concentration of these substances generally bracketing the threshold limit value, or TLV (approximately 0.5, 1.0 and 3.0 times the TLV). The detector was placed in the bottom of the test chamber which was purged with zero air. It remained in this clean atmosphere for at least 24 hours prior to the beginning of the test. Accurately known volumes of pure solvents were injected into the test chamber *via* the septum using a microlitre syringe. The volume of challenge compound required to achieve the desired chamber concentration (*C*) was calculated using the following equation:  $C = (V \times d \times 1000 \text{ mg g}^{-1} \div V_T) \times 24.45 / \text{MW}$  where *C* = parts per million by volume (ppm), *V* = volume of solvent injected (mL), *d* = density of solvent (g mL<sup>-1</sup>), *V<sub>T</sub>* = total volume of the test chamber = 0.01 m<sup>3</sup>, and MW is the gram molecular weight of solvent injected.

The chamber lid was equipped with a small fan underneath the top, two valve-controlled gas inlets, one valve-controlled outlet, and a septum. The fan was operated for approximately 10 minutes at the beginning of the test to ensure homogenous mixing of the gases. It was determined from replicate testing that similar results were obtained whether or not the fan was left on or off during the remainder of the test. The results reported here were obtained with the fan turned off during the test. Temperature and relative humidity were controlled to 24 °C and 34%, respectively. Pressure was measured both inside and outside of the test chamber. Detector readings were recorded every 5–10 minutes for 2 hours. The assumption that the chamber gas or vapor concentration remained constant over the test period was checked at the end of the test using a

**Table 2** Instruments tested and concentrations of challenge chemicals

Challenge chemical	TWA (ppm) <sup>a</sup>	Challenge concentration (ppm)	Detectors tested
Alcohols			
Ethanol	1000	100, 400, 1000	All <sup>b</sup>
Isopropanol	400	100, 250	All
Methanol	200	150, 250	All
<i>n</i> -Propanol	200	100, 260	All
Hydrocarbons			
Isopropyl acetate	250	100, 200	All
<i>n</i> -Hexane	50	29 300	Toxilog, ToxiUltra, Draeger (except H <sub>2</sub> S)
Methane	Simple asphyxiant	22 000	Toxilog, ToxiUltra, Draeger
Propane	1000	12 100	Toxilog, ToxiUltra, Draeger
Styrene	50	10, 50	All
Toluene	50	150, 350	All
Trichloroethylene	50	50, 200	All (except Toxilog SO <sub>2</sub> )
Xylene Mixture	100	50, 100, 150	All
	Methanol: 200		All (except Toxilog SO <sub>2</sub> , Toxilog H <sub>2</sub> S, and ToxiUltra H <sub>2</sub> S)
	Toluene: 150		
	50		
	Xylene: 100		
	100		
Ketones			
Acetone	750	200, 300	All
Cyclohexanone	25	25, 37, 100	All
Methylethylketone	50	100	All
Inorganic gases			
Ammonia	25	18	Toxilog, ToxiUltra (except H <sub>2</sub> S Ultra), Draeger
Carbon dioxide	5000	50 000	Toxilog, ToxiUltra, Draeger
Chlorine	0.5	1, 4	Toxilog, ToxiUltra; Draeger
Hydrogen sulfide	10	8.9	All (except H <sub>2</sub> S)
Nitrous oxide	50	100	Toxilog, ToxiUltra (except H <sub>2</sub> S Ultra), Draeger

<sup>a</sup> 8-hour time weighted average.<sup>14b</sup> See Table 1.

Gastec™ colorimetric detector tube inserted into the test chamber *via* a sampling port. Detector recovery was not systematically monitored following exposure to challenge substances that elicited false positive responses, but it was observed that some of the instruments required up to 24 hours of exposure to zero air to return to a stable baseline. In the case of gases, certified concentrations were introduced into the chamber with gas and air flow rates calculated to result in the desired chamber concentration after 15–20 minutes.

In the case of the highly toxic chlorine tests, detectors were challenged for only 10 minutes *via* a perforated cap fitted over the detector and connected to a gas generator from Advanced Calibration Designs Inc. Model F100 *via* a short length of tubing.<sup>13</sup> Detectors were challenged in a similar fashion from a cylinder of compressed gas certified to contain an accurately known concentration of 8.9 ppm H<sub>2</sub>S.

More than 1200 individual tests were performed. Some of the detector-challenge combinations were not completed because the instrument was unavailable at the time that the tests were run (Table 2).

## Results

Electrochemical signals were subject to positive, negative or no effect depending on the test substance and instrument model. Where there was an effect, it was unequivocal. The time to obtain a signal twice the instrument's detection limit ranged from 0.2–50 minutes, depending on the instrument and level of interfering substance. The time for false positive signals to reach their final readings varied from 10 minutes to over two hours, depending on the instrument and on the challenge chemical. The response was generally linear, but in many cases the test time of two hours was not long enough for the instruments to reach their final readings.

No cross-sensitivities were observed for any of the instruments tested for the following substances, individually: ammonia, carbon dioxide, *n*-hexane, methane, nitrous oxide, propane, toluene, trichloroethylene, or xylene. Cross-sensitivities were observed for some or all of the instruments exposed to the other challenge chemicals, individually: alcohols (ethanol, isopropanol, methanol, *n*-propanol), hydrocarbons (isopropyl acetate, styrene, or a mixture of toluene, xylene and methanol), ketones (acetone, cyclohexanone, methylethylketone (or inorganic gases (chlorine, and hydrogen sulfide). The most noteworthy results are summarized in Tables 3 to 7.

All five models of CO detector were subject to false positives in the presence of ethanol or methanol (Table 3). In general, the Draeger and ToxiUltra CO detectors did not perform as well as the others, being subject also to false positives in the presence of cyclohexanone, isopropanol, *n*-propanol, and styrene. In addition, the Draeger CO detector responded positively to isopropyl acetate, acetone, and methylethylketone.

**Table 3** CO detector responses following 120 minutes of exposure to challenge compounds<sup>ab</sup>

Challenge compound concentration <sup>c</sup>	Biosystems Toxilog	Biosystems ToxiUltra	BW Gas Alert	Draeger Datalogger	ISC TX418
<b>Alcohols</b>					
Ethanol (TWA = 1000 ppm)					
100			<i>d</i>		7
400	3	60	28	139	9
1000	11	150	66	283	50
Isopropanol (TWA = 400 ppm)					
100	<i>d</i>	31	<i>d</i>	11	<i>d</i>
250	<i>d</i>	60	<i>d</i>	60	<i>d</i>
Methanol (TWA = 200 ppm)					
150	23	38	24	220	22
250	36	66	27		39
<i>n</i> -Propanol (TWA = 200 ppm)					
100	<i>d</i>	42	<i>d</i>	15	<i>d</i>
260	<i>d</i>	106	<i>d</i>	74	<i>d</i>
<b>Hydrocarbons</b>					
Isopropyl acetate (TWA = 250 ppm)					
100	<i>d</i>	<i>d</i>	<i>d</i>	4	<i>d</i>
200	<i>d</i>	<i>d</i>	<i>d</i>	12	<i>d</i>
Styrene (TWA = 50 ppm)					
10	<i>d</i>	3	<i>d</i>	2	<i>d</i>
50	<i>d</i>	21	<i>d</i>	29	<i>d</i>
Mixture:					
150 methanol + 150 toluene + 100 xylene	22	27	25	81	20
<b>Inorganic gases</b>					
Chlorine (TWA = 0.5 ppm)					
1	<i>d</i>	<i>d</i>		<i>d</i>	
4	<i>d</i>	<i>d</i>		<i>d</i>	
Hydrogen sulfide (TWA = 10 ppm)					
9	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>
<b>Ketones</b>					
Acetone (TWA = 750 ppm)					
200	<i>d</i>	<i>d</i>	<i>d</i>	18	<i>d</i>
300	<i>d</i>	<i>d</i>	<i>d</i>	32	<i>d</i>
Cyclohexanone (TWA = 25 ppm)					
25	<i>d</i>	5	<i>d</i>	2	<i>d</i>
37	<i>d</i>	7	<i>d</i>	3	<i>d</i>
100	<i>d</i>	27	<i>d</i>	15	<i>d</i>
Methylethylketone (TWA = 50 ppm)					
100	<i>d</i>	<i>d</i>	<i>d</i>	10	<i>d</i>

<sup>a</sup> Reading in ppm CO. <sup>b</sup> TWA<sub>CO</sub> = 35 ppm. <sup>c</sup> Test chamber nominal concentration  $\pm 40\%$ , verified using Gastec™ indicator tubes after 2 hours of exposure. <sup>d</sup> No effect.

**Table 4** H<sub>2</sub>S detector responses following 120 minutes of exposure to challenge compounds<sup>ab</sup>

Challenge compound concentration <sup>c</sup>	Biosystems Toxilog	Biosystems ToxiUltra	ISC TX418 <sup>d</sup>
Alcohols			
Ethanol (TWA = 1000 ppm)			
100	<i>e</i>	<i>e</i>	−1
400	<i>e</i>	<i>e</i>	−1
1000	<i>e</i>		−1
Isopropanol (TWA = 400 ppm)			
100	<i>e</i>	<i>e</i>	−2
300	<i>e</i>	<i>e</i>	−6
500	<i>e</i>	<i>e</i>	−6
Methanol (TWA = 200 ppm)			
100	<i>e</i>	<i>e</i>	−1
150	<i>e</i>	<i>e</i>	−2
<i>n</i> -Propanol (TWA = 200 ppm)			
250	<i>e</i>	<i>e</i>	−6
400	<i>e</i>	<i>e</i>	−14
Hydrocarbons			
Isopropyl acetate (TWA = 250 ppm)			
100	<i>e</i>	<i>e</i>	<i>e</i>
250	<i>e</i>	<i>e</i>	<i>e</i>
Styrene (TWA = 50 ppm)			
10	<i>e</i>	<i>e</i>	<i>e</i>
30	<i>e</i>	<i>e</i>	<i>e</i>
Mixture: 150 methanol + 150 toluene + 100 xylene			<i>e</i>
Inorganic gases			
Chlorine (TWA = 0.5 ppm)			
1	<i>e</i>		
4	<i>e</i>		
Ketones			
Acetone (TWA = 750 ppm)			
200	<i>e</i>	<i>e</i>	<i>e</i>
300	<i>e</i>	<i>e</i>	<i>e</i>
Cyclohexanone (TWA = 25 ppm)			
25	<i>e</i>	<i>e</i>	<i>e</i>
37	<i>e</i>	<i>e</i>	<i>e</i>
100	<i>e</i>	<i>e</i>	<i>e</i>
Methylethylketone (TWA = 50 ppm)			
100	<i>e</i>	<i>e</i>	<i>e</i>

<sup>a</sup> Reading in ppm H<sub>2</sub>S. <sup>b</sup> TWA<sub>H<sub>2</sub>S</sub> = 10 ppm. <sup>c</sup> Test chamber nominal concentration ±40%, verified using Gastec™ indicator tubes after 2 hours of exposure. <sup>d</sup> The instrument displayed negative readings (−15 to −20 ppm) after the first 15 to 20 minutes of exposure. It stabilized at the levels indicated 1 to 2 hours following initial exposure to the challenge compound. <sup>e</sup> No effect.

The ISC instrument was the only H<sub>2</sub>S detector subject to negative responses in the presence of alcohols, exhibiting an important decrease after 15 to 20 minutes and a long period of stabilization (Table 4).

**Table 5** NO detector response following 120 minutes of exposure to challenge compounds<sup>abc</sup>

Challenge compound concentration <sup>d</sup>	Biosystems ToxiUltra
Ethanol (TWA = 1000 ppm)	
100	<i>e</i>
400	−4
1000	−23

<sup>a</sup> Reading in ppm NO. <sup>b</sup> TWA<sub>NO</sub> = 25 ppm. <sup>c</sup> No effect observed when challenged with the following: isopropanol, methanol, *n*-propanol, hydrocarbons (isopropyl acetate, styrene), ketones (acetone, cyclohexanone, methylethylketone), inorganic gases (chlorine, hydrogen sulfide), or a mixture of methanol, toluene and xylene. <sup>d</sup> Test chamber concentration ±40%, verified using Gastec™ indicator tubes after 2 hours of exposure. <sup>e</sup> No effect.

The only false positive response observed for the ToxiUltra NO detector was for ethanol at a concentration higher than 100 ppm (Table 5). It responded initially to *n*-propanol, but returned to baseline after approximately 15 minutes.

The Toxilog and ToxiUltra NO<sub>2</sub> detectors exhibited false positives in the presence of chlorine, and negative responses in the presence of hydrogen sulfide (Table 6). Both the Toxilog and ToxiUltra NO<sub>2</sub> detectors initially responded to carbon dioxide, methane and nitrous oxide challenges, but the responses returned to baseline levels after approximately 15 minutes. A similar, short period of instability was observed when the ToxiUltra NO<sub>2</sub> detector was challenged with *n*-hexane.

The Toxilog and BW Gas Alert SO<sub>2</sub> detectors exhibited false positives in the presence of styrene (Table 7). The ISC SO<sub>2</sub> detector responded negatively when challenged with 30 ppm of styrene and with a mixture of hydrocarbons and alcohol, decreasing to a minimum of −23 ppm after 10 minutes before stabilizing at −6 ppm after 95 minutes.

## Discussion

This study has revealed cross-sensitivities for electrochemical detectors used in air monitoring that are undocumented by the

**Table 6** NO<sub>2</sub> detector response following 10 minutes of exposure to challenge compounds<sup>abc</sup>

Challenge compound concentration <sup>d</sup>	Biosystems Toxilog	Biosystems ToxiUltra	BW Gas Alert
Inorganic gases			
Chlorine (TWA = 0.5 ppm)			
1	1.4	1.4	
4	6.7	6.1	
Hydrogen sulfide (TWA = 10 ppm)			
8.9	−1.9	−9.7	<i>e</i>

<sup>a</sup> Reading in ppm NO<sub>2</sub>. <sup>b</sup> TWA<sub>NO<sub>2</sub></sub> = 3 ppm. <sup>c</sup> No effect observed when challenged with the following: alcohols (ethanol, isopropanol, methanol, *n*-propanol), hydrocarbons (isopropyl acetate, styrene), ketones (acetone, cyclohexanone, methylethylketone), or ammonia.

<sup>d</sup> Gas concentration passing over the detector directly from a certified cylinder of compressed gas using a similar setup to that used for instrument calibration. <sup>e</sup> No effect.

**Table 7** SO<sub>2</sub> detector response following 120 minutes of exposure to challenge compounds<sup>abc</sup>

Challenge compound concentration <sup>d</sup>	Biosystems Toxilog	Biosystems Toxiultra	BW Gas Alert	ISC TX418
Hydrocarbons				
Styrene (TWA = 50 ppm)				
10	0.2		2	0.2
50	6	0.2		5.6
Mixture:				
150 methanol + 150 toluene + 100 xylene	<sup>e</sup>		<sup>e</sup>	–6

<sup>a</sup> Reading in ppm SO<sub>2</sub>. <sup>b</sup> TWA<sub>SO<sub>2</sub></sub> = 2 ppm. <sup>c</sup> No effect observed when challenged with the following: alcohols (ethanol, isopropanol, methanol, *n*-propanol), isopropyl acetate, ketones (acetone, cyclohexanone, methylethylketone), or inorganic gases (ammonia, hydrogen sulfide). Note: The BW Gas Alert and the ISC TX418 were not tested with chlorine. <sup>d</sup> Test chamber nominal concentration  $\pm 40\%$ , verified using Gastec™ indicator tubes after 2 hours of exposure. <sup>e</sup> No effect.

manufacturers. Responses elicited by interfering substances in the absence of target chemicals ranged from 10–500% of the target chemical TLV. Such cross-sensitivities can lead to erroneous conclusions regarding worker exposures to target chemicals which may, in fact, be altogether absent. False responses varied between manufacturers for detectors measuring the same target chemical. Detector responses also varied depending upon both the concentration of the challenge chemical and exposure time. Detectors exhibiting a linear response to substances other than the intended target analytes cannot be used to monitor such interferents, however, since their sluggish response times make them insensitive to fluctuating levels of such substances.

There are two cases where none of the electrochemical detectors tested should be used: (1) the measurement of CO in the presence of methanol or ethanol; and (2) the measurement of NO in the presence of ethanol. In other cases, where false responses were observed, an alternative instrument can be selected that would not be affected by the cross-sensitivity.

A more comprehensive study is required to understand the underlying processes resulting in the observed cross-sensitivities and to quantify their effects. Differences between instruments may be due to differences in electronic circuitry design or in the sensors used in the instruments by the different manufacturers. Most instrument manufacturers purchase the electrochemical cell from another supplier and build the electronics to process the signal. For example, detectors manufactured by *BW Technologies*, *Industrial Scientific Corporation* and *Biosystems Incorporated* all use the same electrochemical cell, *Citcel*, manufactured by *City Technology Incorporated*.<sup>15,16</sup> Other manufacturers, such as *Draeger*, manufacture their own electrochemical cells. Manufacturers claim electrochemical cell detection limits of 1 ppm for the CO, H<sub>2</sub>S, and NO cells, and 0.5 ppm for the NO<sub>2</sub> and SO<sub>2</sub> cells. Performance between instruments using the same sensor may vary as a result of differences in the instrument manufacturers' designs. This may include differences in different models of the same sensor from the same manufacturer, the electronics used to process the signal, the membranes and the filters used, the flow, the software, *etc.* The manufacturers' product literature

describes response times to target analytes of 20–60 seconds, operating temperatures of –40 to 0 °C at the lower end of the range to 40–50 °C at the upper end of the range, and operating relative humidities of 0–15% at the lower end of the range to 90–99% at the upper end of the range.<sup>7–11</sup>

Electrochemical detectors can be very useful for monitoring exposures to toxic vapors and gases. Manufacturers claim a linear response and, when used properly under appropriate conditions, they may offer good selectivity, repeatability and accuracy. However, a survey of potentially interfering substances present at levels below their TLVs, including substances undocumented by manufacturers, must precede exposure assessments performed using electrochemical detectors. Potential bias can be avoided by careful selection of instrument type and model.

## Conclusion

The present study demonstrated that, in the absence of target analytes, electrochemical detectors may give false positive readings that are undocumented in manufacturers' literature. Following such a response, detectors may require up to 24 hours exposure to a clean atmosphere before returning to baseline. A follow-up study is needed to evaluate the performance of electrochemical detectors where the target analyte is present in combination with the interferents identified in the present study. Based on the results of the present study, future experiments should include tests to determine detector response to: (1) CO in combination with isopropyl acetate, acetone, cyclohexanone, ethanol, isopropanol, methanol, methylethylketone, *n*-propanol, or styrene; (2) H<sub>2</sub>S in combination with cyclohexanone, ethanol, isopropanol, methanol, or *n*-propanol; (3) NO in combination with ethanol; (4) NO<sub>2</sub> in combination with chlorine, or hydrogen sulfide; and, (5) SO<sub>2</sub> in combination with styrene, or a mixture of methanol, toluene and xylene.

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