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End of Service Life Indicator (ESLI) for Respirator Cartridges. Part I: Literature Review

George Favas

Human Protection & Performance Division
Defence Science and Technology Organisation

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ABSTRACT

One of the critical elements related to efficiency and safe use of respirator filter cartridges is their operational life span. Predicting the life span of a respirator cartridge is difficult because it is dependant on parameters such as environmental temperature, the nature and concentration of the contaminants and the rate of breathing. Ideally, respirator cartridges should include an End of Service Life Indicator (ESLI) system to warn the wearer when it is time to change cartridges.

The development of a cheap, reliable, disposable ESLI would significantly improve the protection of military units in a chemical warfare (CW) environment. Currently, no ESLI is available on the market that is capable of detecting a range of CW agents and toxic industrial chemicals (TICs) and therefore, the commercialisation potential of a successful ESLI is high. This report reviews all prior art relating to ESLIs for respirator cartridges which will provide the foundation for future development in this area.

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Executive Summary

One of the critical elements related to efficiency and safe use of respirator filter cartridges is their operational life span. Predicting the life span of a filter cartridge is difficult because it is dependent on parameters such as environmental temperature, relative humidity, the nature and concentration of the contaminants and the rate of air passing through the filter. In many cases the first indication that the filter cartridge has reached saturation is the odour of the pollutant. Unfortunately, this type of practise is very dangerous because the odour thresholds of many pollutants are above the acceptable exposure limits. Ideally, respirator filter cartridges should include an End of Service Life Indicator (ESLI) system to warn when it is time to change filters.

Although, the concept of an ESLI for respirator cartridges is not new, no ESLI is available on the market that is capable of detecting both chemical warfare (CW) agents and toxic industrial chemicals (TICs). The integration of a cheap, reliable, disposable micro-chemical sensor would significantly improve ADF protection in a CW environment by warning the user when the effectiveness of their respirator cartridge is about to expire. Furthermore, this ESLI technology could be transferred to civilian respirator units and to other ADF Platform equipment such as NBC protective ensembles, air monitoring equipment and all other filtering systems. Subsequently, the commercialisation potential of a successful ESLI is very high.

A comprehensive literature review on the history of respirator cartridges containing an ESLI is provided in this report. This information will provide the foundation for future development in the art of ESLI system.

Authors

George Favas
Human Protection & Performance Division

George Favas graduated from Monash University with a B.Sc (Hons) in 1995, and with a PhD degree (Science) in 2000. He is also about to submit a M. Eng Sc thesis and has concurrently almost completed a M. Bus Sys at the same University. He worked as a Post-doctoral Research Fellow in Chemistry (2000 – 2002) and in Chemical Engineering (2002 – 2003) at Monash University. For more than nine years, George managed a number of innovative scientific and engineering projects for the power generators in the Latrobe Valley, Flinders Power (South Australia), within several CRCs, and for a number of national and international mining companies including Alcoa, BHP, Shell Australia, Rio Tinto and NEDO (Japan). Furthermore, he has collaborated in research in the US, Japan, Indonesia and Germany and has presented lectures at some of the world's most prestigious universities. In September 2003, George joined Defence Science and Technology Organisation (DSTO) where he continued to work on carbon products and on developing chemical micro-sensory devices.

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1. Introduction

Respirators using replaceable filter cartridges are commonly used for protection against a wide range of respiratory hazardous materials which include toxic and/or disease producing dusts, mists, sprays, fumes, vapours or gases. While these devices provide excellent protection against hazardous materials, their protection capabilities diminish with use and eventually permit the passage of the hazardous agents unless the filter cartridge is replaced.

One of the critical elements related to efficiency and safe use of these cartridges is their operational life span. Predicting the life span of a respirator filter cartridge is difficult because it is dependant on parameters such as environmental temperature [1-3], relative humidity [4-14], the nature and concentration of the contaminants [15-26] and the rate of breathing [26-31]. In many cases the first indication that the cartridge has reached saturation is the odour, taste or irritation from the pollutant [32-34]. Unfortunately, this practise is highly dangerous because the odour thresholds of many pollutants are above the permissible exposure limit [35, 36]. Health organisations recommend administrating a cartridge change schedule, however these programmes can be tedious and time consuming [37]. Ideally, respirator cartridges should include an End of Service Life Indicator (ESLI) system to warn the wearer when it is time to change cartridges.

An ESLI system for respirator cartridges can be categorised as either passive or active indicating systems. Passive indicator systems typically include chemically coated paper strips, which change colour when the sorbent material is near depletion. A major advantage with passive indicators is that they are relatively cheap to incorporate into a respirator cartridge. However, the major disadvantages with most passive indicators are that they require active monitoring by the user, observations can only be conducted with sufficient lighting and the indicators are generally only specific towards a particular chemical functional group.

In contrast, active indicator systems incorporate electronic sensors to monitor the presence of contaminants and an indicator (either visual or audible signal) to provide an automatic warning to the user. Most active indicator systems have the advantage of being less selective towards specific chemicals and therefore can be used in a range of different environments, however a major limitation to these systems is the cost to manufacture.

A comprehensive literature review on the history of respirator cartridges containing ESLIs is provided in this report. This information will provide the foundation for future development in the art of ESLIs for respirator cartridges.

2. Literature review

2.1 Passive End of Service Life Indicators

End of Service Life Indicators (ESLIs) on respirators is not a new concept. After World War I, Yablick [38, 39] patented a canister with a built in colour indicating system for measuring the residual life of the canister (Figure 1). Yablick proposed that indicator paper or solution specific to the "poisonous or obnoxious gas" [38, 39] could be incorporated onto the side of the canister.

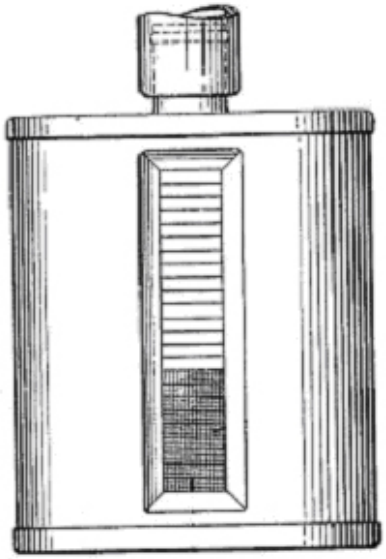

Figure 1: Indicating gas-mask canister (Yablick [38], 1925)

Dragerwerk in 1957 [40] took out a German patent on a colourimetric indicator located in the line of sight of the user, inside the interior space of the mask. The drawback to this design was that it only warned the user when a significant concentration of harmful agents had already entered inside the facemask.

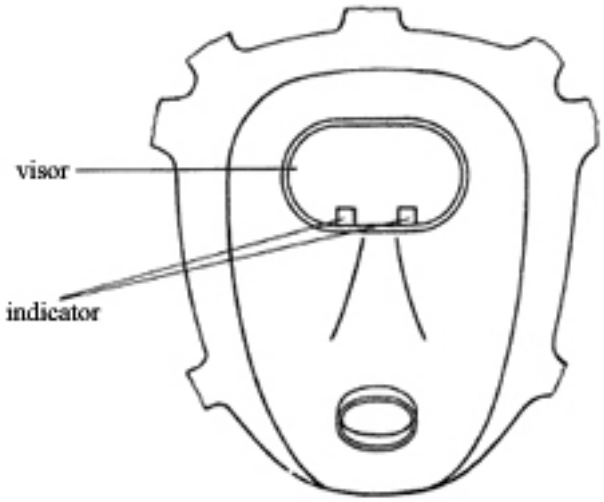

Figure 2: Dragerwerk's patent with the indicator located inside the face mask [40].

In 1960, Wiswesser [41] invented a window indicator assembly for gas mask canisters for detecting moisture or vapours. The unique design of the canister's window were the two half discs which made up the indicator. One half of the disc was permanent in colour while the other half contained the indicator paper. When both colours matched, the service life of the canister was spent. A similar ESLI principle is currently being used by North Safety Products (see Section 2.2).

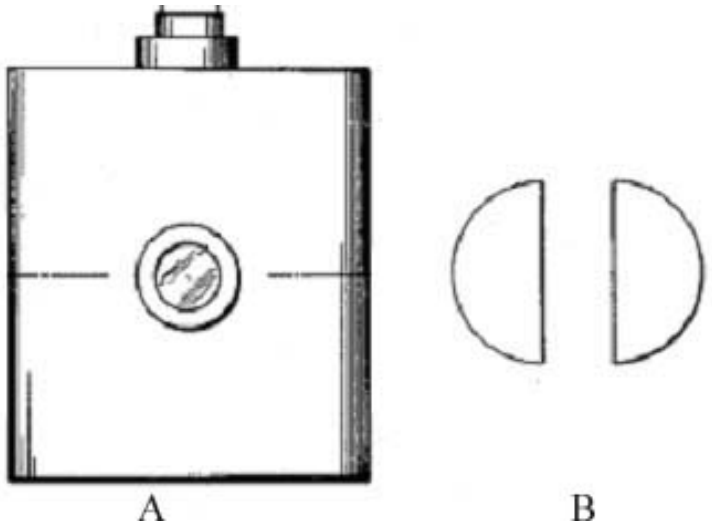

Figure 3: The Wiswesser canister, 1960 [41], (A) canister with window indicator assembly (B) two half discs making up part of the ESLI.

Similarly, Roberts [42] in 1976 designed a colourimetric indicator for detecting the end of service life of a canister for filtering vinyl organo materials (Figure 4). The devices of Yablick [39], Wiswesser [41] and Roberts [42] used indicators supported by thin opaque carriers such as strips of paper, activated alumina or the cartridge sorbent itself so that only a portion of the indicator against the window was visible. Similarly, Wing's

respirator patent in 1982 also included an indicator strip, located horizontally across the canister [43].

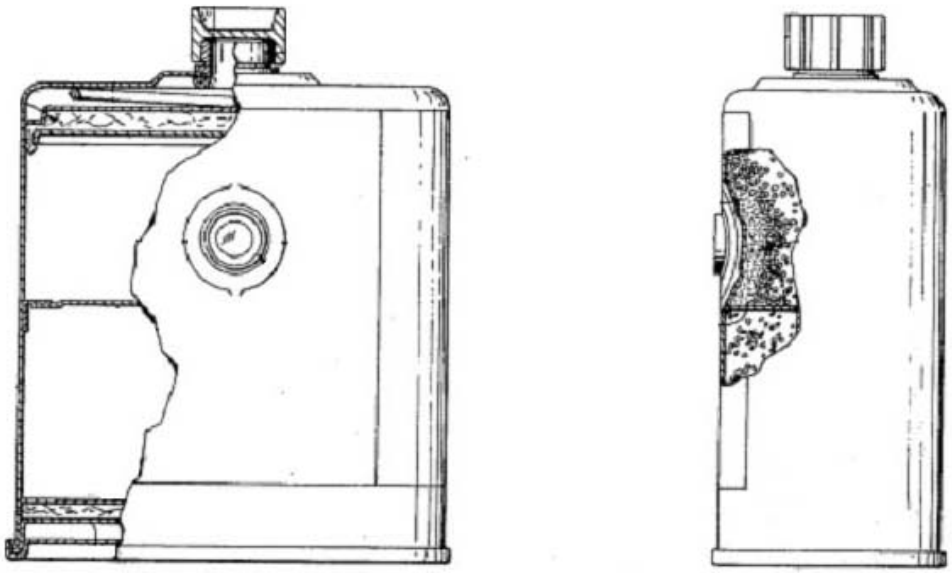

Figure 4: Colourimetric vinyl chloride indicator (Roberts [42], 1976)

In 1978, Auergesellschaft GMBH patented [44] a supplementary filter attachment for increasing the operational efficiency, effectiveness and hence the service life of respirator cartridges (Figure 5). This supplementary attachment contained a drying agent in front of the filter bed and a colourimetric window for indicating when this drying agent was spent. This patent claimed to increase the residual life of the catalyst contained inside the respirator cartridge however the major drawback to this design was that it did not notify the user when the main respirator itself was completely spent.

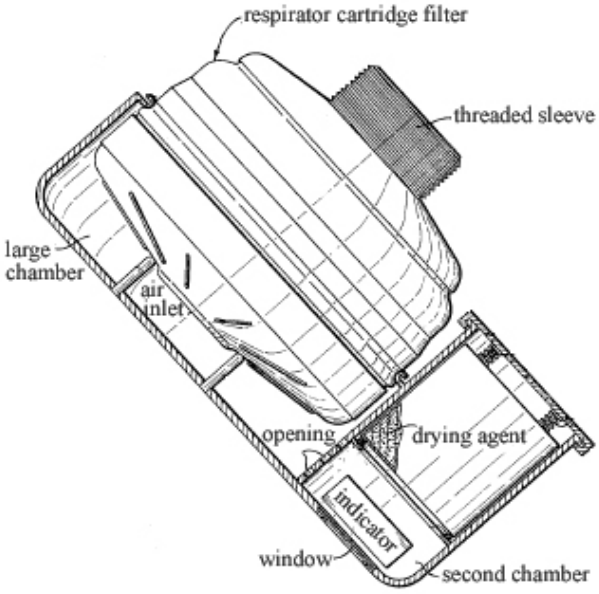

Figure 5: Auergesellschaft GMBH's supplementary filter attachment containing a drying agent and colourimetric indicator [44].

In 1979, McAllister et. al [45] patented an ESLI on a filter mask for vinyl chloride monomers. This patent was similar to the Roberts patent [42] however the major difference was the addition of manganese (IV) oxide (MnO_2) to the potassium permanganate ($KMnO_4$) indicator in the McAllister et. al patent [45]. The presence of MnO_2 with $KMnO_4$ was claimed to give a better colour contrast from start to finish thereby making the indicator much easier to read.

The American Optical Corporation in 1979 took out several patents for cartridge ESLIs. Their first invention [46, 47] was similar to Yablick [39] however its specific use was for both water-soluble and water-insoluble organic vapours. In this patent, sodium or potassium dichromate ($K_2Cr_2O_7$) gave a colour change in the presence of aromatics, chlorinated compounds and aliphatic ketones. The visual indication that the cartridge service life had ended was designed to occur before the threshold limit value (TLV) had been exceeded (Figure 6). Unfortunately, a major problem with this design was the shelf life of the ESLI was considerably shorter than the cartridge sorbent [48]. Tanaka et. al [48] reported that 2 years after manufacture, the indicator changed colour despite the cartridge not being worn, consequently these cartridges were not approved in Japan [49].

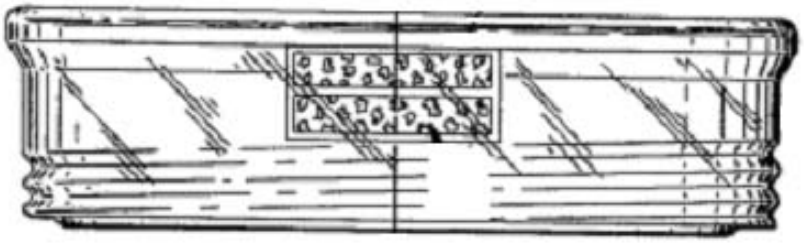

Figure 6: ESLI for organic vapours (American Optical Corporation [46, 47], 1979)

In 1985, the American Optical Corporation updated their patent to include a sieve material to the indicator, whose sole function was to selectively adsorb water [50]. The dried chemical agents were found to give faster response times, better resolution in the colour change on the ESLI and a significant improvement on the shelf life of the indicator.

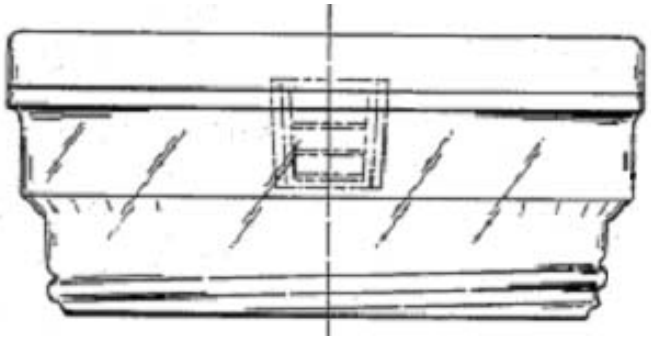

Figure 7: The addition of a drying compartment before the indicator improved sensitivity towards the end of service life of the cartridge (American Optical Corporation [50], 1985)

Eian in 1981 [51, 52] used a colourimetric indicator sheet positioned along the inner transparent sidewall of the respirator cartridge (Figure 8). The novelty of this invention was the transparent sidewall, which allowed the indicator to show the remaining capacity of the entire sorbent bed rather than the condition of a small volume near the indicating window.

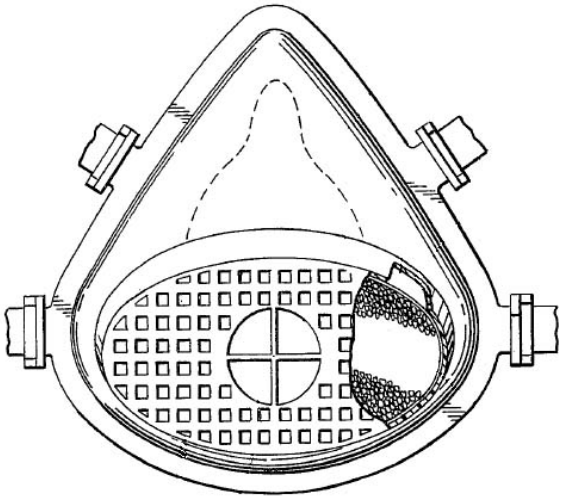

Figure 8: Respirator design of Eian [52] with built in indicator sheet.

In 1984, TNO patented [53] a gas mask module for detecting poisonous organophosphates (eg insecticides, nerve agents etc) using an enzyme (butyryl cholesterinase). The method of operation involved attaching the module at the end of a gas mask and after a certain suction time had elapsed, the module was detached and a second liquid reagent was released from inside the module. The non-decolourisation of the second reagent was an indicator that the threshold concentration had been exceeded. The obvious drawbacks to their module design include the lack of a real time, passive monitoring; the cost of replacing a new module with every subsequent test; and the annoyance of being forced to remove the module from the mask in order to conduct a threshold level test.

In 1986, Dragerwerk [54, 55] patented a respirator cartridge design equipped with a colourimetric indicator (Figure 9). The uniqueness of this design was the small chamber located between the adsorbent bed and the upper void space, which contained the indicator. A magnifying glass positioned on the external wall of the cartridge assisted viewing colour changes in the indicator and the progression of air through the flow indicator. Furthermore, this patent postulated that several of these chambers could be immersed at different depths inside the adsorbent bed for providing a chronological progression of hazardous vapours through the cartridge.

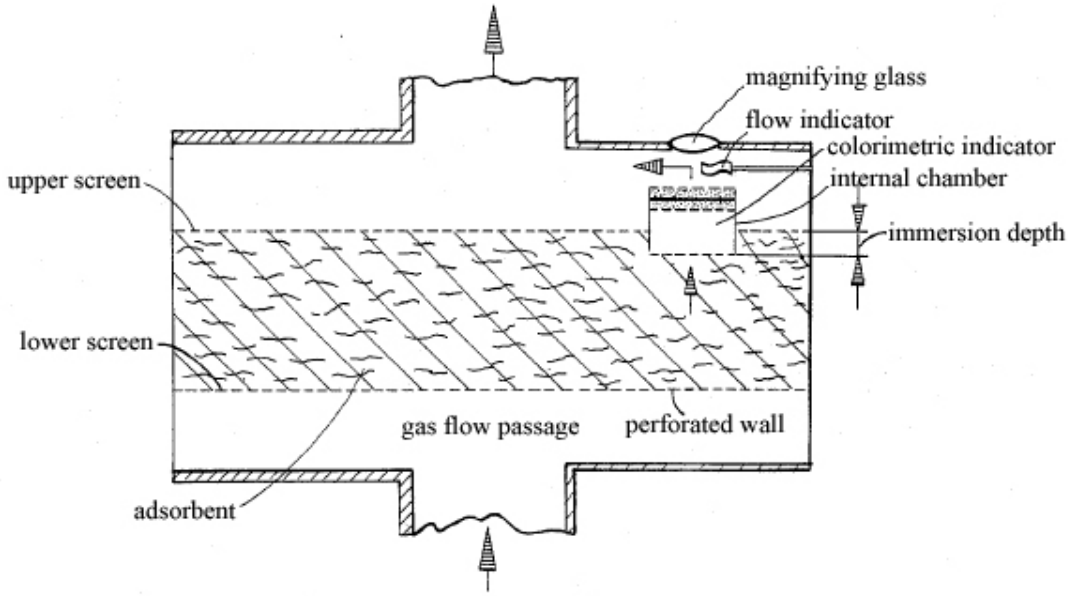

Figure 9: Colourimetric indicator chamber inside respirator cartridge (Dragerwerk, 1986 [54])

In 1994, Draegerwerk [56] improved the detection device from their 1957 patent [40] by designing a system that prevented toxic gases from reaching the indicator strip before the face mask was worn and allowed the activation of the indicator strip while wearing the face mask. However, similar to their 1957 patent, the design does not provide adequate warning because the colourimetric change only occurs when toxic gases have already entered the facemask.

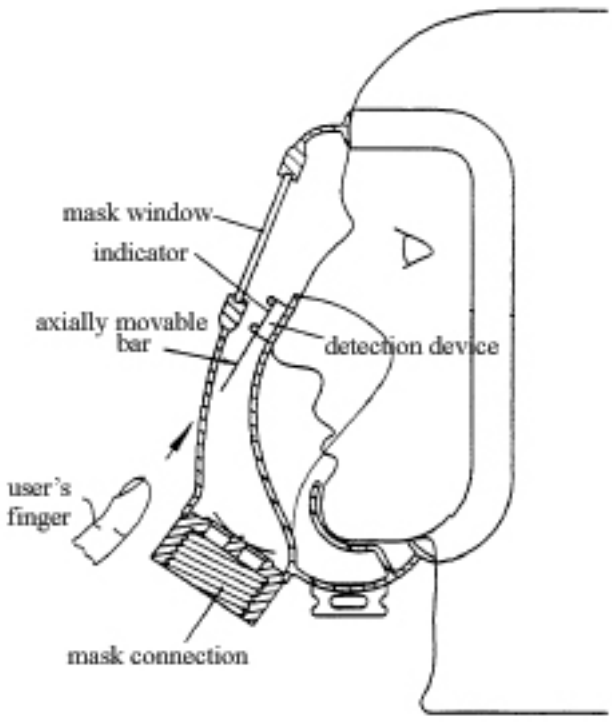

Figure 10: Draegerwerk's breathing mask with an indicator signalling penetration of a toxic substance into the mask [56].

In 1995, Haddington [57] took out a World patent on a respiratory filter indicator (Figure 11). The unique aspect of Haddington's design was the positioning of the indicator (composed of an activated alumina which had been impregnated with an indicator (eg potassium permanganate)) in between the facemask and respirator cartridge.

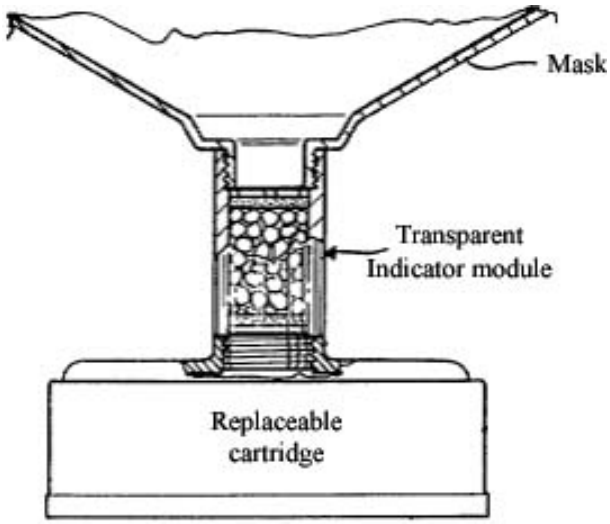

Figure 11: Indicator module attached to a filter cartridge and mask [57]

In 2002, North Safety Products took out several patents on a "respirator cartridge with service life indicator" [58, 59]. Similar to Yablick's design in 1925 [38], the North Safety Products patent used a strip of indicator paper to detect the presence of acidic agents. The major difference to the North Safety Products' invention was the cartridge's mechanistic design, which allowed the wearer to continuously rotate the cartridge in the one direction until the colour changing display was in the line of sight.

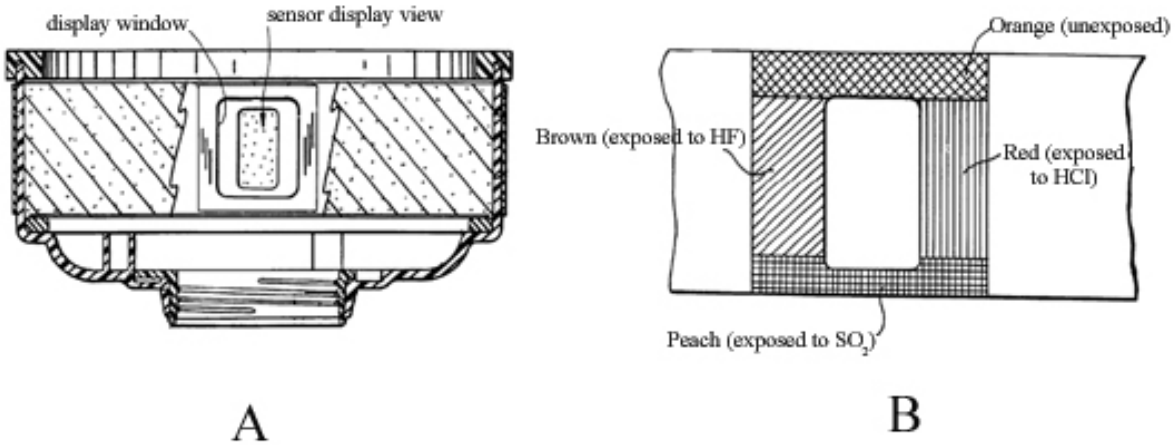

Figure 12: The ESLI system patented by North Safety products (A) cartridge and position of the paper indicator (B) colour changes associated with particular acidic agents [58].

Recently in 2003 and 2004, Scentczar Corp (US) [60, 61] patented a simple, low-cost, residual life indicator badge for measuring the remaining life of adsorbent beds towards volatile organic compounds. Their design involved a concentric pattern containing a colourimetric indicator that was indexed to match the residual life of an adsorbent bed. Scentczar Corp claimed that this badge could also be applied to

respirator cartridges, however a major problem to this claim is that the residual life on the indicator badge may not adequately match the remaining life of their respirator cartridge. That is, the rate of breathing by different people, in particularly during different periods of activity, will not be the same.

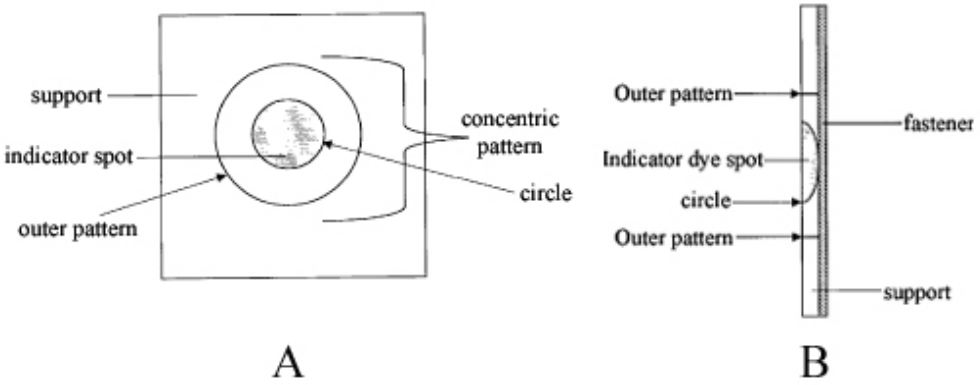

Figure 13: Scentczar Corp'S residual life indicator (A) front view (B) side view

While these patents provide important historic advancements in the art of ESLIs, there still remains a need for greater sensitivity to cartridge sorbent exhaustion and the ability to be used in a range of toxic environments.

2.2 Commercially available passive colourimetric ESLI respirator cartridges

In 1998, the Occupational Safety and Health Administration (OSHA) recommended that employers provide respirators equipped with a National Institute for Occupational Safety and Health (NIOSH) certified ESLI for the expected contaminant or to implement a cartridge change schedule to ensure that the cartridges are replaced before contaminant breakthrough occurred [62].

In February 2002, many respirators containing passive ESLI were withdrawn from the market because the indicator on the cartridge was not visible while wearing the full face piece [63].

Currently, North Safety Products is the only company offering more than one respirator cartridge containing an ESLI. Currently four respirator cartridge types suitable for organic vapours, acidic (i.e. HCl, HF, SO_2, H_2S), basic (i.e. ammonia) and/or mercury/chlorine environments are being sold (Table 1). The design of the respirator cartridges is very similar to their patents (see passive indicator systems; Section 2.1) which allows the cartridge to be continually rotated in the one direction until the indicator is visible from the face piece.

Table 1: Commercial respirators with built in ESLIs by North Safety Products [64]

Respirator	Description
	Organic vapour (Toluene Diisocyanate)
	HCl, HF, SO_2, H_2S
	Ammonia
	Mercury, chlorine

One of the major drawbacks to the North Safety ESLI design is its limitation to detect only a few selected chemical functional groups. Consequently, this respirator ESLI would not be adequate when multiple hazardous chemicals with different functional groups are present [65].

2.3 Non colourimetric passive indicators

A unique ESLI concept suggested by Wollin et. al [66] in 1932 for indicating the exhaustion of filters was to use a substance, which, when exposed to an air impurity, would release a chemical that a user could detect by its taste or smell. In this patent, the example of hydrocyanic gas penetrating through a filter bed could be detected by using nicotine to produce a characteristic odour, which would subsequently notify the user to change filter.

Similarly, Wing [43] in his 1982 canister patent also suggested that the release of stimulant as a warning device for canister expiration however, details of the chemicals involved in this process were not disclosed in the patent.

In 1998 TNO [67] further developed this concept and patented an odourant, to notify the user (by smell) that the respirator cartridge was about the expire (Figure 14). The patent claimed that when organic vapours and dangerous substances are adsorbed into the respirator and come into contact with the odour impregnated active carbon, the odorant becomes displaced from the carbon and is passed along with the air to the user [67-69]. The user recognises the smell as an indicator thus signifying the respirator is about to lose its effectiveness.

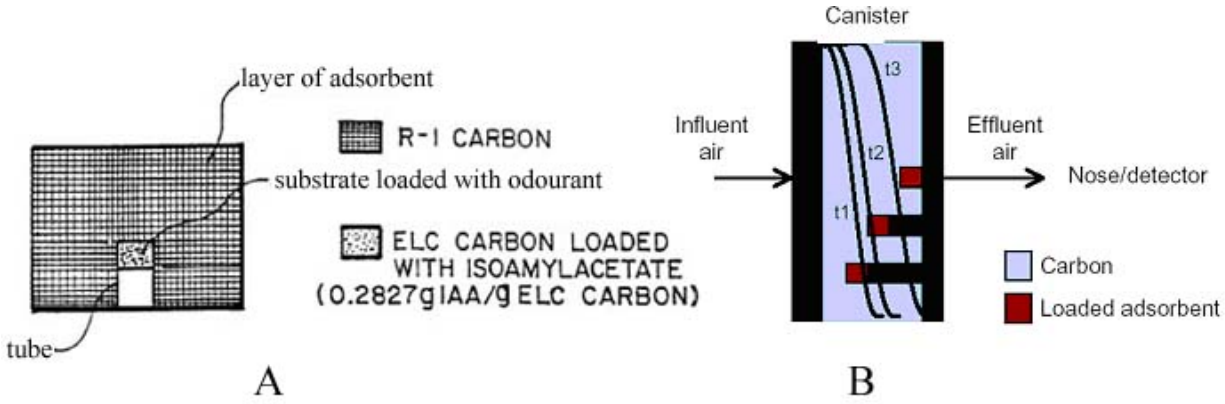

Figure 14: Side view of the respirator cartridge (A) patents [67, 68] (B) Linders [70]

Despite this indicator concept being unique to the art of respirator ESLI, there still remains doubt on the user's adequate timely disposal of the respirator cartridges. Human factors such as individual olfactory sensitivity under different breathing rates and under different health conditions (eg nasal passages blocked because of a cold), individual placebo effects and diminished olfactory sensitivity towards repeated exposure to the odorant, could result in early or late disposal of the respirator cartridges. Early disposal of respirator cartridges will in turn increase the operational costs in replacing the cartridges whereas, late disposal could potentially result in hazardous inhalation of the agent. Furthermore, user doubts on respirator effectiveness may hinder user confidence and performance under hazardous conditions.

2.4 Active End of Service Life Indicators (AESLI)

AESLI systems are comprised of electronic components to monitor the level of contaminants and a visual or audible signal to provide an automated warning to the user.

In 1965, Loscher [71] developed a mechanical-electrical alarm device for detecting organic vapours inside air purifying canisters. In this design, wax was applied to join two wires that supported a spring inside the probe. In the presence of organic vapours, the wax lost its strength and released the spring to activate an alarm light. The likely drawbacks to this design were its complexity and its potential for false alarms due to changes in environmental temperature.

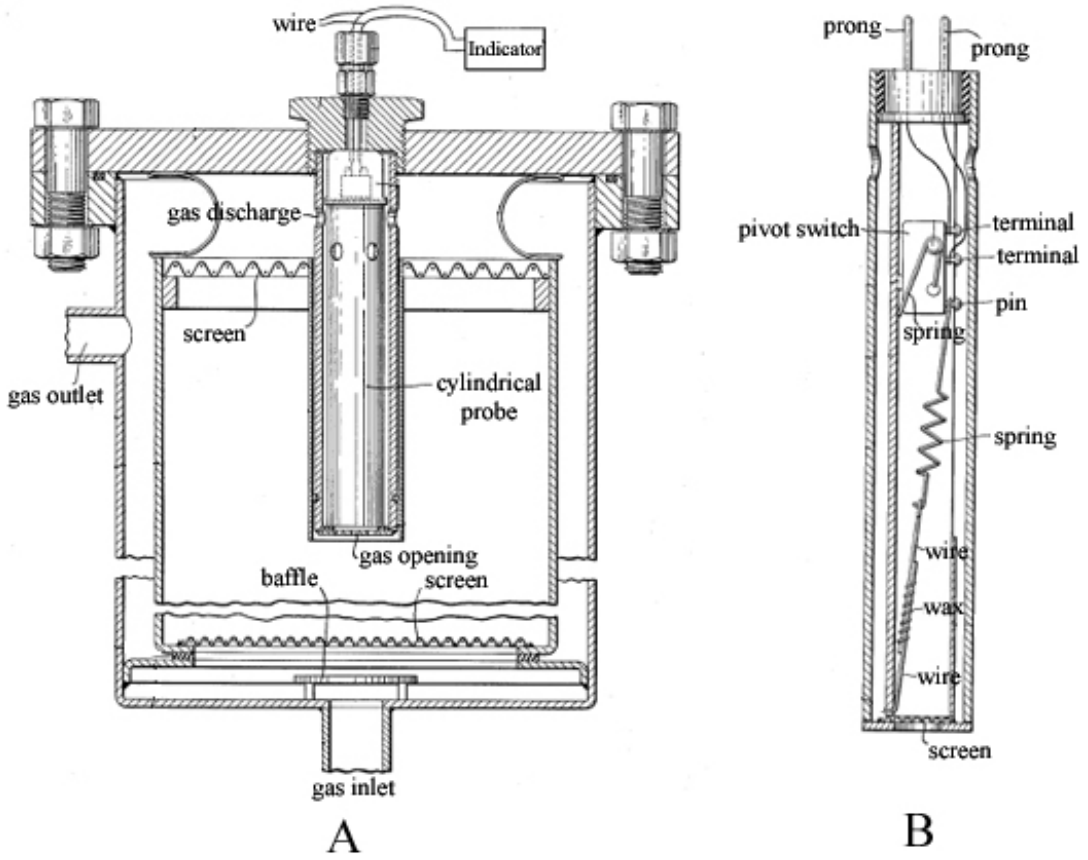

Figure 15: Loscher's mechanical-electrical ESLI [71] (A) the respirator canister (B) the cylindrical probe.

In 1973, Wallace's first patent [72] measured the remaining capacity of an oxygen-producing canister by applying an electrode into the canister's potassium superoxide adsorbent bed. Oxygen producing canisters have been patented elsewhere [73-78] however Wallace's unique design measured changes in electrical resistance with increasing water adsorption and an alarm was triggered when the sorbent material was almost completely saturated. The major drawback to this design was that oxygen-producing canisters have relatively short life spans (eg ~25 min) whereas carbon based canisters can be operated for much longer periods (dependant predominantly on the concentration of contaminants being filtered).

In 1975, Wallace's second [79] patent was an electronically actuated safety alarm system for detecting the presence of toxic gases (eg acid, acid precursor and alkyl halide) (Figure 16) by measuring changes in the electrical resistance of nitrogen containing polymers. The presence of toxic gases was found to convert the nitrogen containing polymers into quaternary ammonium salt groups, which significantly reduced the electrical resistance measured by the electrode. Furthermore, the author claimed that the active indicator could be integrated into respirator cartridges by drilling a hole in the cartridge wall and mounting the electrode into the activated carbon component.

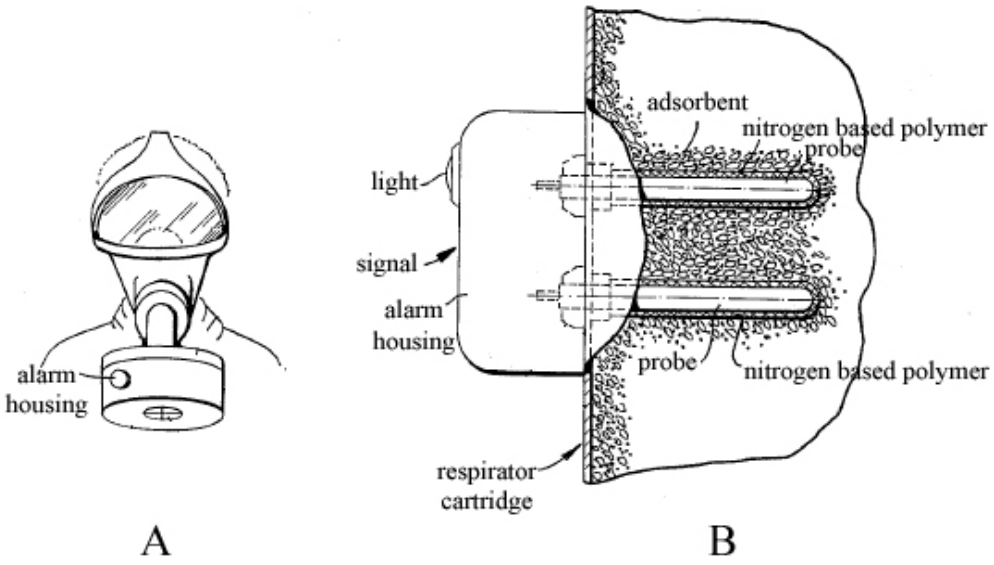

Figure 16: Electronic alarm system for detecting hazardous gases by measuring changes in the electrical resistance of nitrogen based polymers (A) respirator cartridge (B) detector system

Also in 1975, Wallace was awarded his third patent [80] on a respirator alarm system for detecting the presence of toxic gases. In this design, two electrodes (at least one electrode coated with an electrically insulating material of low melting point (eg wax)) were positioned into the carbon filter bed (Figure 17). The patent claims that in the presence of toxic gases, heat is generated in the carbon bed, which subsequently melts the wax to complete an electrical circuit between the electrodes through the charcoal. The alarm is then activated on completion of the electrical circuit.

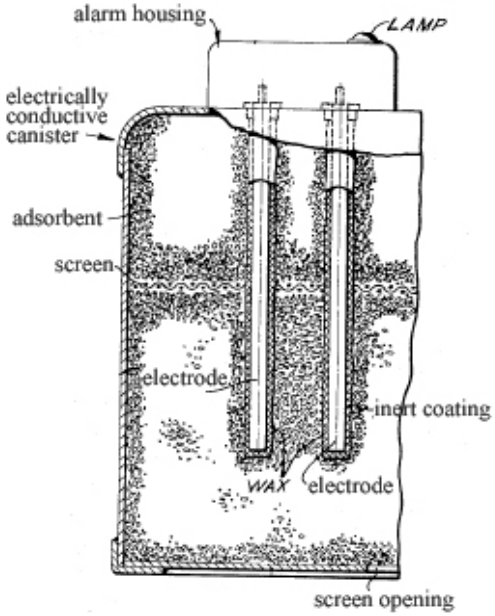

Figure 17: Wallace's thermally activated warning system for respirator canisters [80].

In 1978, NIOSH selected a metal oxide gas sensor (MOGS) to act as service life indicator for organic vapour air purifying respirators [81]. The MOGS was chosen on the basis of its low cost, commercial availability and its desirable non-specificity to a large number of organic vapours. The drawback to the MOGS was the large current drain caused by the relatively high operational temperature (~200°C).

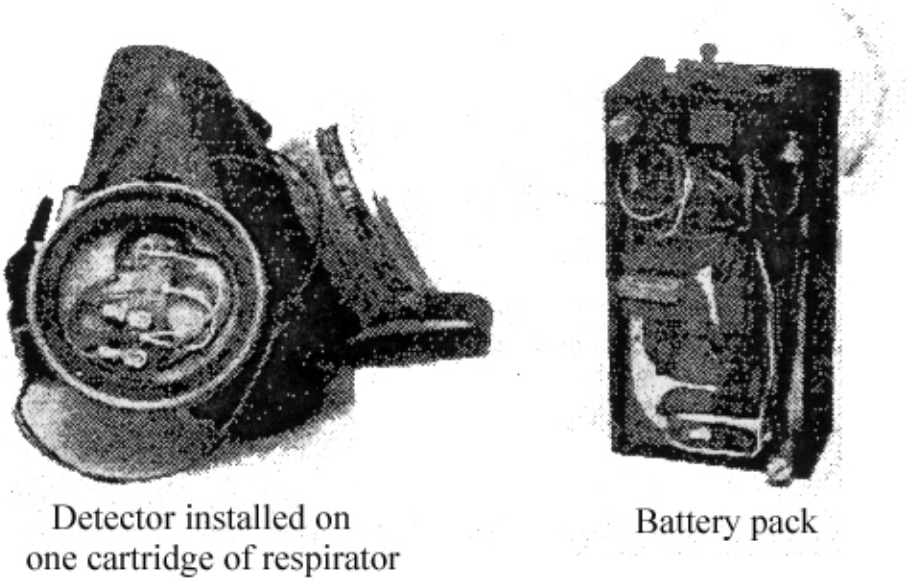

Figure 18: NIOSH's prototype ESLI containing a metal oxide gas sensor on one side of the respirator cartridge.

In 1979, the American Optical Corporation patented [82] an exothermic sensor located in the cartridge adapter or in the facemask cavity (Figure 19). The backbone to this invention (similar to Wallace's thermally activated warning system [80]) was the heat released when a gas becomes adsorbed onto the surface of the activated charcoal. This sensor subsequently monitored the heat evolved during adsorption of the gas into the adsorbent. The patent reported a significant amount of heat can be generated, typically 10° - 15°C for organo-chloride agents adsorbing onto activated charcoal. The invention design also incorporated a reference element to cancel out signals caused by ambient temperature fluctuations thus eliminating false alarms. A major disadvantage to the design was that during periods of low concentration, prolonged agent exposure, the charcoal adsorbent became saturated and differential temperature changes could not be detected to trigger the alarm.

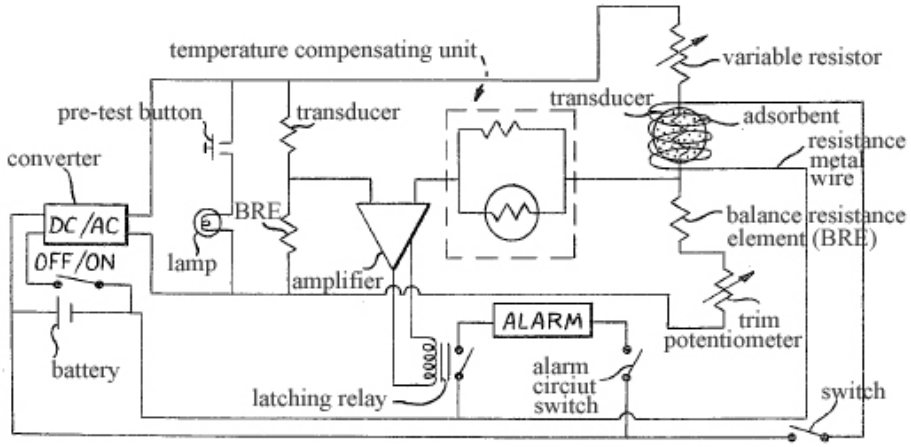

Figure 19: Electronic circuit diagram for detecting the cartridge's end of service life [82]

In 1984, NIOSH recommended that AESLIs should provide an advanced warning to the user when 90 percent of the cartridge is expended [83].

In 1989, Auergesellschaft GMBH patented [84, 85] a respirator cartridge attachment containing a warning device that was capable of detecting dangerous gases using standard electrochemical measuring cells (Figure 20). The proposed warning cartridge was designed to fit in between the facemask and respirator filter cartridge (Figure 21). The electrochemical measuring cells continually measured the concentration of toxic gases (eg carbon monoxide, chlorine, hydrogen sulfide and hydrogen cyanide) and an alarm (visual and audible) was triggered when the level of these toxic gases had reached above a predetermined concentration. A likely drawback to this design is that toxic gases could only be detected once filter breakthrough had occurred therefore, the system may not comply with NIOSH recommendations because it does not provide adequate warning for the user to evacuate from the hazardous environment and change cartridges.

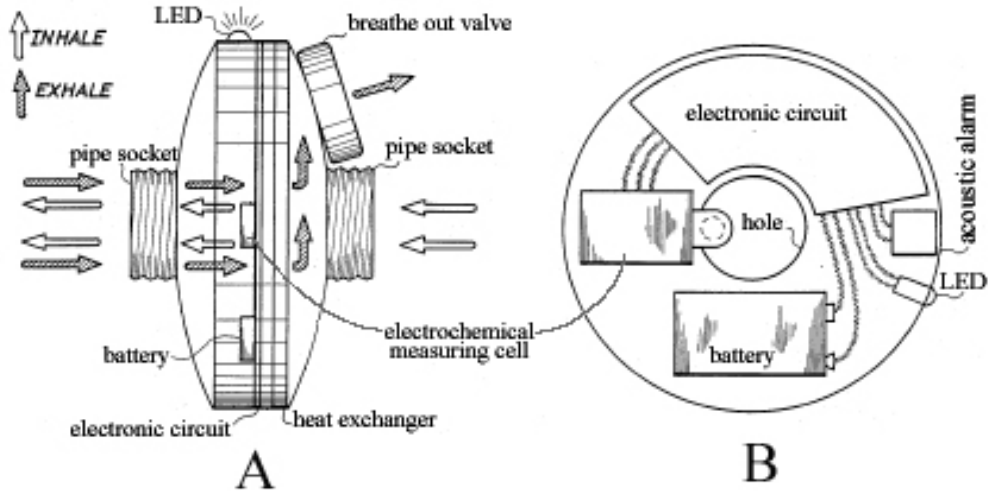

Figure 20: Auergesellschaft GMBH's respirator shaped warning device containing electrochemical sensor [84, 85] *(A) side view (B) top view.*

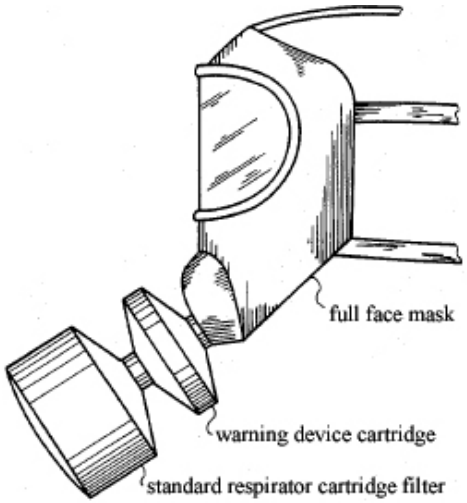

Figure 21: Auergesellschaft GMBH's warning device positioned between face mask and respirator cartridge filter [84, 85]

In 1989 Stetter took out a US patent [86] and in 1990 was awarded a German patent [87] on a chemiresistor sensor device for respirator cartridges (Figure 22). This indicator device gave a real-time warning on the extent of absorbent saturation by measuring the electrical conductivity of a chemically reactive coating. The patent proposed that this sensor advantageously gave a generic response to many contaminants inside the filter cartridge and that the sensor unit required marginal power at room temperature. In addition, the patent claimed that an electronic compensated bridge circuit design could minimise baseline shifts from changes in ambient conditions, such as temperature and relative humidity.

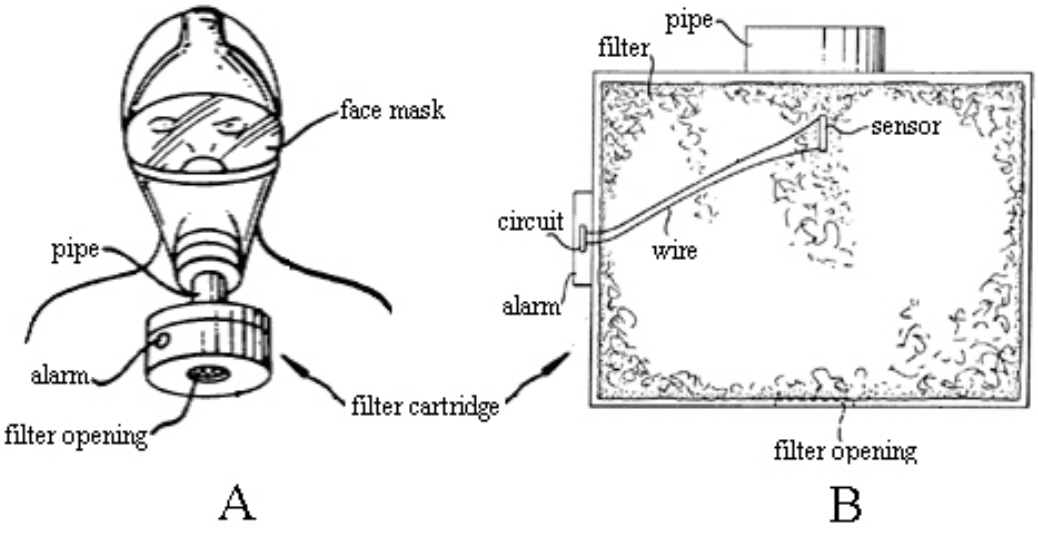

Figure 22: Stetter's design [87] (A) face mask and respirator cartridge (B) respirator cartridge with chemiresistor sensor.

In 1991, Stetter repositioned the alarm from the side of the respirator cartridge (Figure 22) to the front of the face mask (Figure 23). This new position did not obstruct the user's vision and was clearly visible when flashing [88] (Figure 23). In 1993, Stetter's group [89] reported that chemiresistor sensors were suitable for detection of organic vapours such as ethyl acetate however further improvements in the stability and sensitivity were necessary.

Stetter later patented the chemical gas sensor for the respirator cartridge in 1996 [90]. In this patent Stetter claimed that changes in electrical impedance resulting from changes in a vapour sensitive polymer could be utilised to detect the presence of organic vapours.

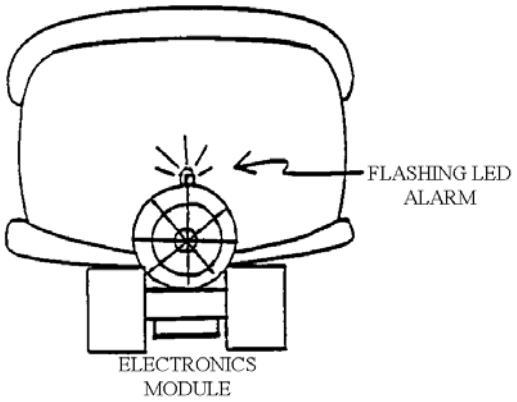

Figure 23: Schematic of the prototype ESLI mounted on a full fask mask [88].

In 1991, Geraetebau GMBH [91] incorporated several gas sensors (Figure 24) located behind the filter cartridge on positive pressure gas masks. This indicator system monitored the changes in gas electrical resistance, voltage or capacitance and an alarm was triggered when the levels were outside predetermined limits. Unfortunately, it is unlikely that this system could be incorporated into a stand-alone negative pressure respirator unit (eg the S10 respirator unit) because of its high-energy demand, its high cost of manufacture and its cumbersome size.

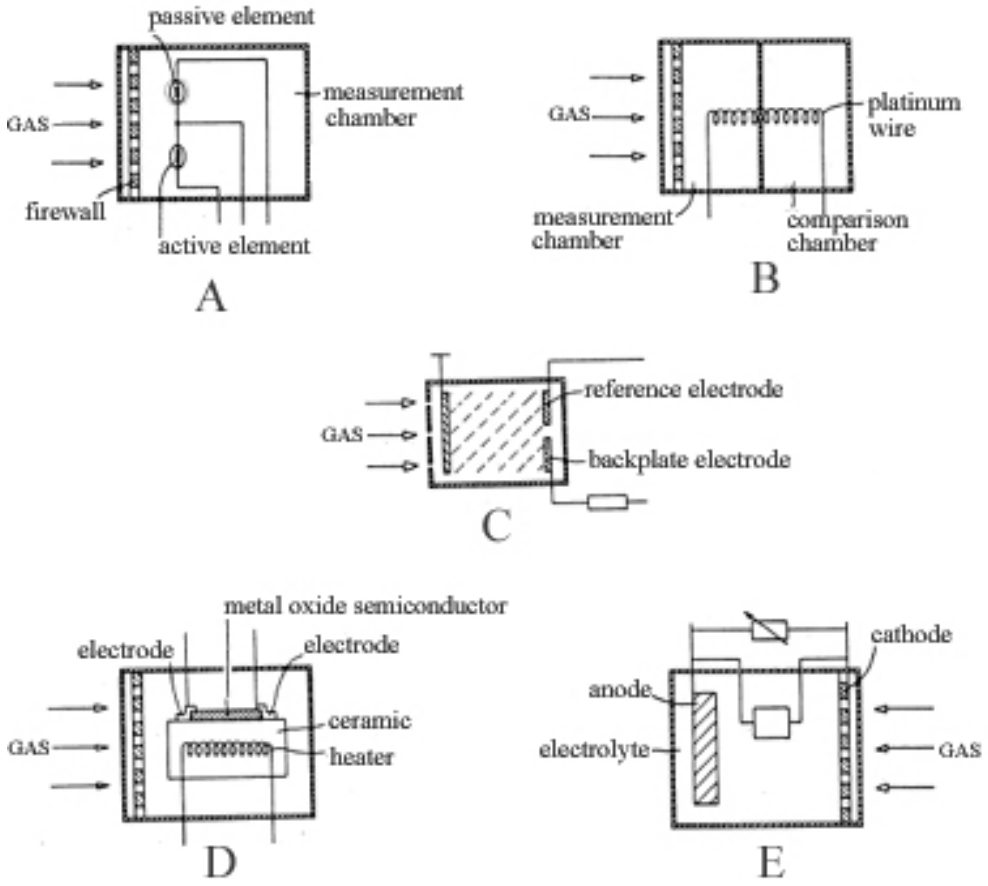

Figure 24: The five sensors proposed by Geraetebau GMBH's positive pressure gas mask [91] *(A) explosive sensor based on the principle of "heat of reaction" or "catalytic combustion" (B) thermal conductivity sensor (C) an electrolytic "redox based" carbon monoxide sensor (D) semiconductor sensor for toxic chemicals (E) an electrolytic "redox based" oxygen concentration sensor*

In 1994 Dragerwerk [92], patented a mask and respirator unit which controlled the passage of inhaled air through an indicator. The indicator simultaneously registered the retention effect of the filter and the sealing effect of the edge of the mask. Furthermore, this patent proposed the use of a miniaturized computer chip-like indicator system capable of detecting pollutants at different levels. The indicator system itself was anticipated to consist of a light source and detector. The light intensity (measured in transmission or reflection) was a measure of the amount of pollutant received by the indicator.

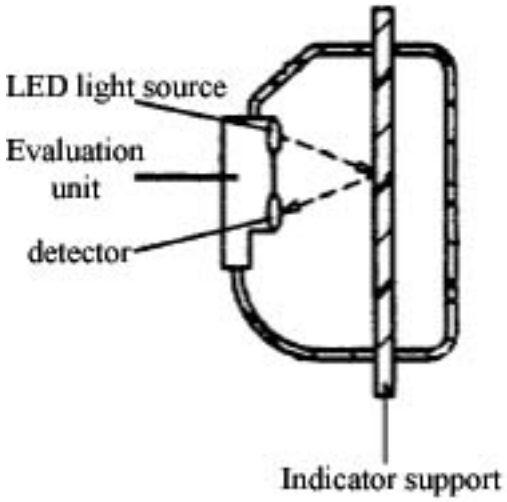

Figure 25: Electronic indicator system using a light source and detector [92]

The Minnesota Mining and Manufacturing Company (3M Company) took out a World patent in 1996 [93] and US patent in 1997 [94] on a very sophisticated respirator ESLI. The unique aspect of this invention was the air sampling device attached to the side of the respirator. Air passing through the sorbent material was constantly sampled and processed to give an active indication (eg audio, visual or tactile response) to the concentration signal. The signalling rate of the indicator varied as a function of target species concentration.

The invention also allowed interchanging of exposure indicators for detecting alternative agents without interfering with the flow of air through the respirator. Furthermore, the processing device was capable of being removed from the respirator to measure the concentration of the target species in the ambient air and then replaced back onto the respirator to measure the concentration of the agent flowing through the cartridge. In addition, a range of complex sensors could be attached to the respirator unit for monitoring the concentration of hazardous agents.

The only limitation to this unit design was the positioning of the indicator directly behind the respirator cartridge, which could be potentially dangerous if the cartridges were not immediately replaced after the indicator had alarmed. Furthermore, it is uncertain whether this ESLI system satisfies the NIOSH recommendations [83] in notifying the user when the cartridge had reached 90% saturation, thus allowing the user sufficient time to change cartridge or to evacuate from the hazardous environment.

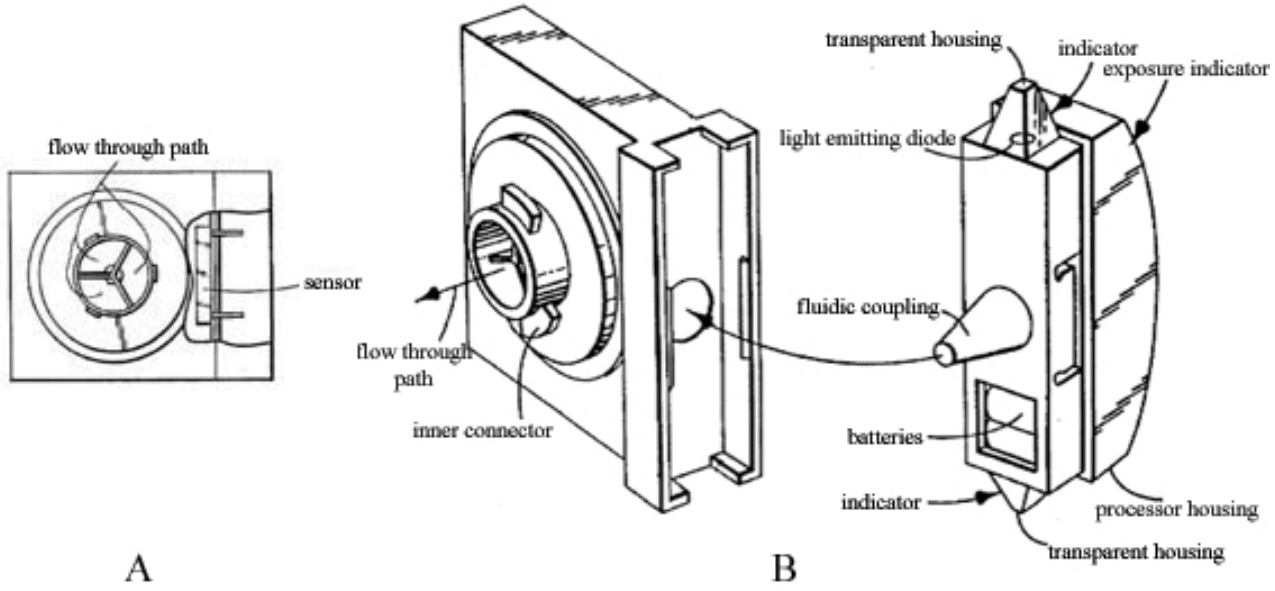

Figure 26: Air sampling ESLI [93]

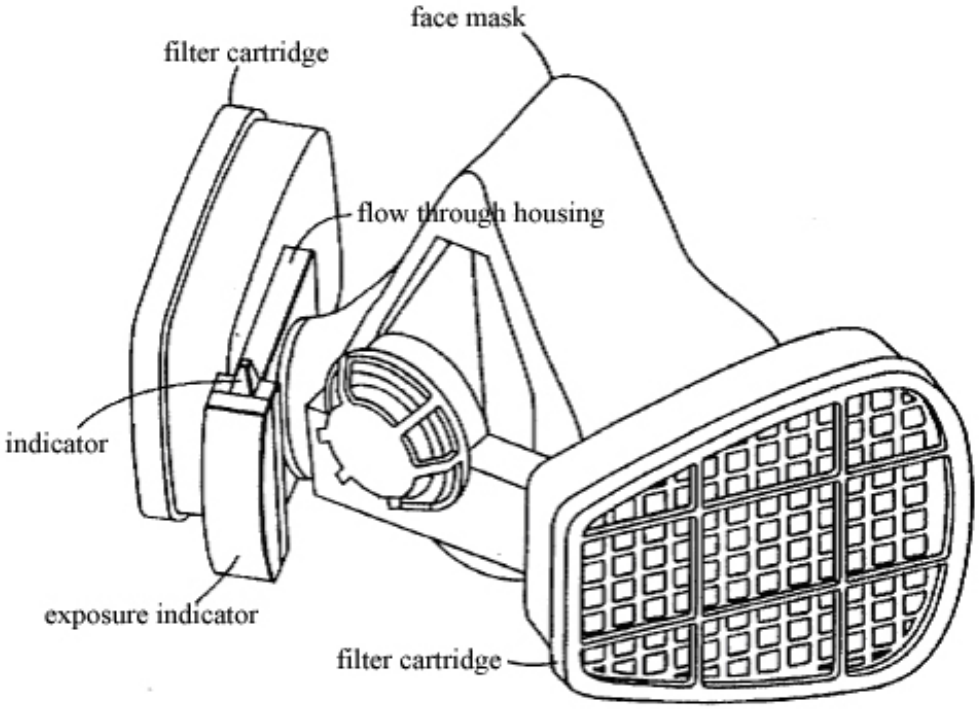

Figure 27: Position of the ESLI relative to the face mask and respirator cartridges [93]

Bernard et. al [95-96] took out a European patent in 1998 [95], World patent in 1999 [96] and US patent in 2002 [97] on a respirator cartridge containing a relatively simple fibre optic chemical sensor (FOCS) for indicating the end of service life of the unit. The indicator concept design appeared to be similar to the Dragerwerk patent [92]. That is, when the light intensity measured by the detector fell below a predetermined level, an alarm was triggered signifying gas/vapour saturation and the expiration of the cartridge. Bernard et. al [95, 96] claimed that this approach for the detection of hazardous materials was more universal than any prior ESLI because the indicator was not selective and worked with all products susceptible of being absorbed by activated carbon and by the porous silica (Figure 28 and Figure 29). That is, when the porous silica became saturated, the light intensity passing to the detector decreased.

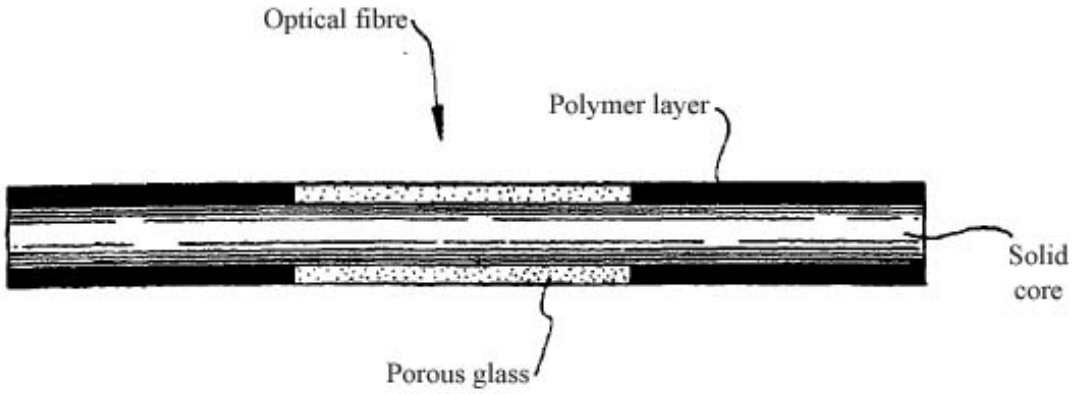

Figure 28: Fibre optic containing a microporous glass section (surface area ~250m²/g) [95].

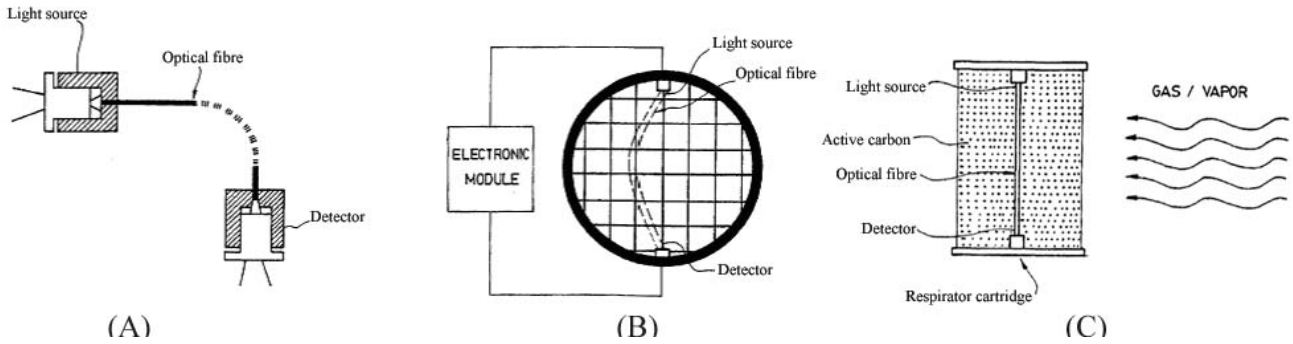

Figure 29: Fibre optic chemical sensor (FOCS) for respirator cartridge (A) FOCS with light source and detector (B) electronic module connected to FOCS, (C) sensor connected inside respirator cartridge [95].

Furthermore, the Bernard et. al patent [95, 96] used relatively cheap and common electrical components (i.e. phototransistor detector, electrolight diode in the infrared region (800nm) and a LED alarm. The simplicity of this design, the relatively low cost to manufacture and its effectiveness to detect a range of hazardous components are attractive features to the commercialisation of this respirator ESLI design.

Gordik [98] in 2001 was granted a Russian patent on a gas mask and respirator design for determining the time of protective action from mercury vapours. The inventor claimed an increased efficiency and simplified construction design for measuring the amounts of mercury aerosol passing through the filter. The drawback to this ESLI device was that it could not operate in other toxic environments.

In 2001, the Health and Epidemic Prevention Station in the Peoples Republic of China patented a filter-mask with an expiry indicator suitable for organic toxic gases. The unique feature of this respirator design was the electronic gas sensory device, which alarmed when the canister had become saturated with the adsorbed organic gas [99]. The respirator design positioned the sensor directly behind the respirator cartridge (similar to the 3M patent in 1997) and an auditory alarm system positioned on the side of the cartridge (Figure 30). Unfortunately, the type of sensory system for the detection of chlorinated hydrocarbon vapours was not disclosed in the patent.

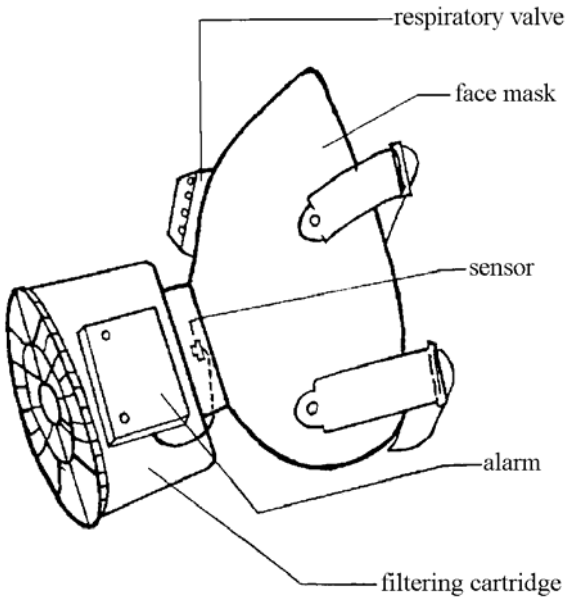

Figure 30: Filter mask with expiry indicator for organic gases [99]

In 2002, Shigematsu et. al [100] also patented a gas mask with the sensor positioned between the respirator cartridge and face mask (Figure 31). This Japanese patent detected the presence of organic gases electronically by monitoring colourimetric changes of the indicator paper located inside the cartridge. Furthermore, an LED light connected from the sensor and the warning device (Figure 31) notified the wearer when it was time to change cartridge. The patent claimed the warning system incorporated in the cartridge met Japanese approval standards.

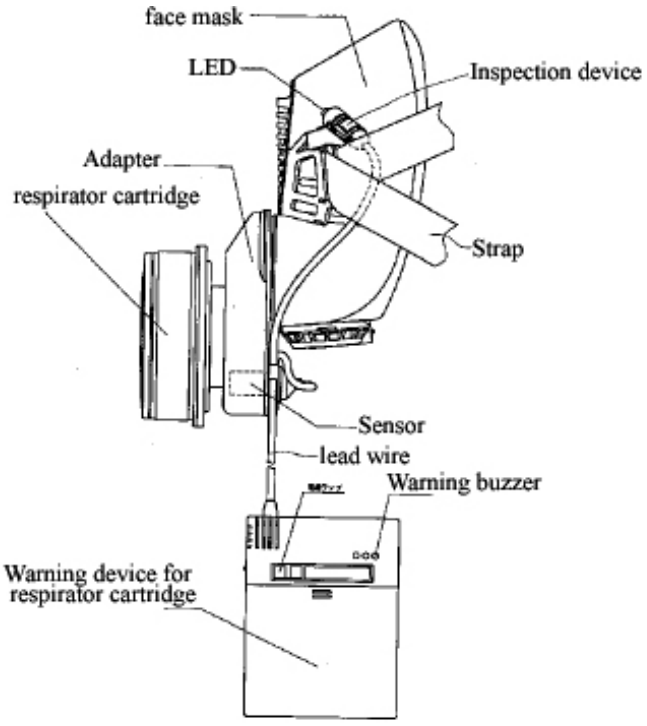

Figure 31: Schematic of a Japanese respirator ESLI for organic gases [100]

In 2003, Hori et. al [101] tested a respirator containing a commercially available semiconductor gas sensor. The device (Figure 32) appears to be very similar to the Shigematsu et. al [100] Japanese patent (Figure 31). Hori et. al [101, 102] reported that breakthrough of organic vapours could be detected at various humidities however early detection of chlorinated hydrocarbons (eg chloroform) was less successful. Furthermore, the major drawbacks to this electronic ESLI design include a high power consumption (6V); a low effective operational time (6 to 8 hours); a high running cost (i.e. replacement of batteries); and a cumbersome size that may restrict worker effectiveness.

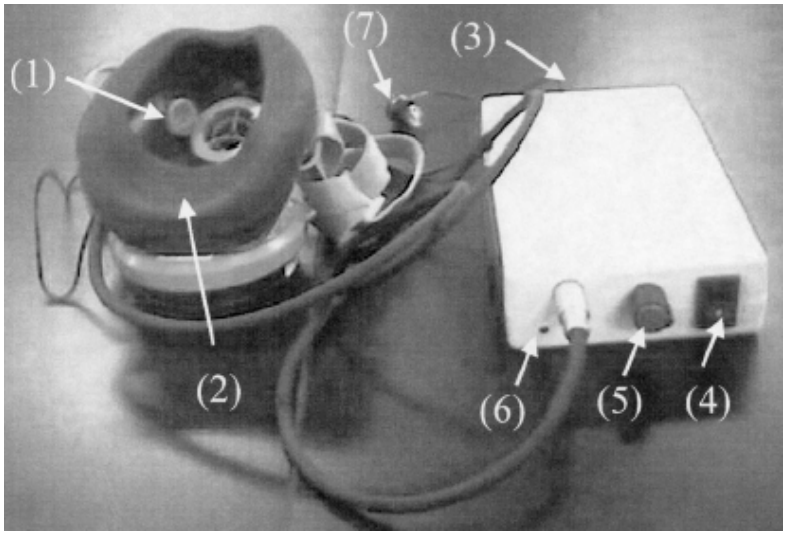

Figure 32: Hori et. al's respirator design. (1) semiconductor sensor, (2) covering, (3) control box with alarm system, (4) power switch, (5) sensitivity knob, (6) alarm indicator, (7) earphone[101].

2.5 Current research on ESLIs

Several organisations are currently developing active ESLIs and are subsequently being tested in defence institutions around the world.

Scentcar Corporation is currently evaluating an active residual life indicator for detecting the build up of volatile organic carbons (VOCs), using a semiconductor sensor [103] (Figure 33). This semiconductor sensor measures the concentration of the contaminant on the carbon bed (via changes in electrical resistance) and subsequently estimates its remaining capacity. In contrast, the semiconductor Active ESLI patents of Wallace in 1975 [79] and Stetter in 1990 [87] (see Section 2.4) did not measure contaminant concentration but instead alarmed to the presence of the contaminant.

Figure 33: Scentcar Corporation's Active ESLI [103]

The likely limitations of Scentcar Corporation's active sensor would be portability, cost and high power consumption. This active sensor is currently being tested at the US Naval Research Laboratory (NRL) [103].

Cyrano Sciences in the US have commercialised a handheld "electronic nose", called the Cyranose® which has the capacity to discriminate between closely related gases/vapours. The backbone to Cyrano Sciences's electronic nose is an array of 32 carbon black-organic polymer composite chemiresistor sensors [104]. In the presence of a gas/vapour, these sensors respond creating a pattern across the array, which is identified using pattern recognition software [105]. Similar chemiresistors are currently being investigated as ESLIs and as residual life indicators for respirator cartridges and for full body protection gear [106] (Figure 34). The US NRL is also currently evaluating Cyrano Sciences's chemiresistor technology [106].

Figure 34: Cyrano Science's prototype residual life indicators [106] (A) chemiresistors for respirator cartridges (B) the integration of chemiresistors or electronic noses to full body protection gear (C) electronic nose chip

The US Army Edgewood Chemical and Biological Centre (ECBC) and the US NRL are currently investigating surface acoustic wave (SAW) sensors, chemiresistor sensors (CR) and photo-ionization detectors (PID) as possible respirator ESLI [107]. Preliminary tests have shown that these sensor technologies can detect dimethyl methylphosphate (DMMP), a nerve agent simulant [107, 108]. Further information regarding the mode of operation of these chemical microsensors is covered in Part II, in this series of reports.

Furthermore, ECBC and NRL are currently evaluating colourimetric indicator films [109], patented by ChemMotif Inc. [110], to qualitatively detect the presence of various organic vapours in a carbon bed [107]. The novelty of these indicator films is that they employ a displaceable dye to indicate the presence of organic vapours. A colour change occurs when the dye becomes displaced by the contaminant and diffuses into a receiving layer where it can be seen (Figure 35). These chemical indicator films are currently being tested on a broad class of chemical warfare agents and toxic industrial chemicals.

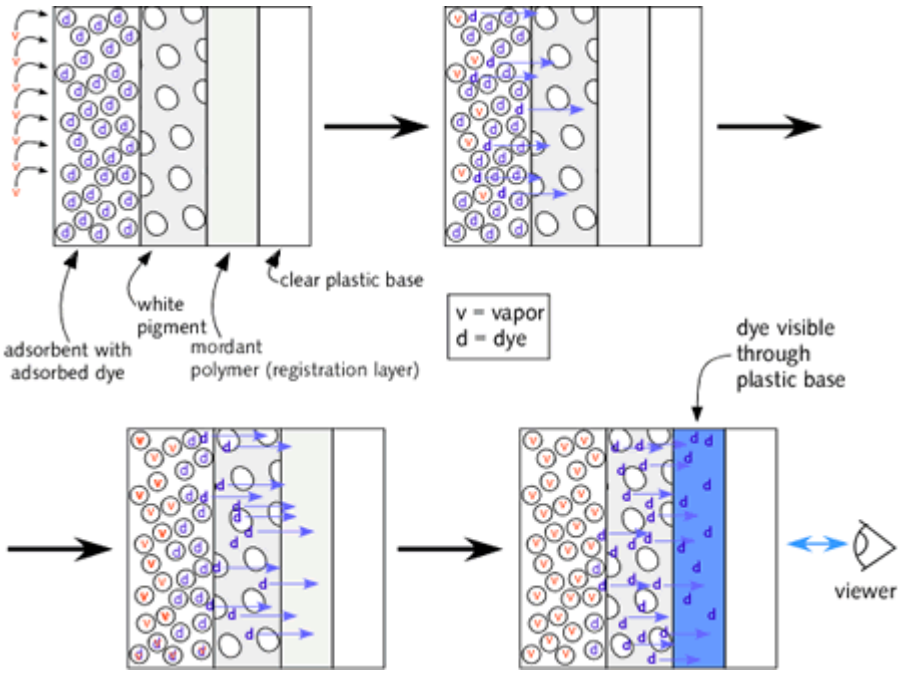

Figure 35: Schematic of ChemMotif's dye desorption process [110, 111]

TNO is the fourth organisation that is currently performing research on ESLIs. The backbone to TNO's respirator ESLI patent in 1998, was the desorption of an odorant from a selected region within the carbon bed, which subsequently notified the user (by smell) that the cartridge was about to expire (see Section 2.3). The limitations to this original design included differences in individual olfactory sensitivity and individual placebo effects towards the odorant (see Section 2.3). Consequently, TNO has been developing an optochemical sensor for detecting "the release of a so-called signal compound" [112] (Figure 36). Instead of an odorant, a fluorescent indicator dye is released from the carbon, which is then detected by the optochemical sensor, and an alarm is subsequently triggered. Furthermore, this device contains a pulsed LED and time-gated circuitry, which significantly reduces the energy consumption of the unit.

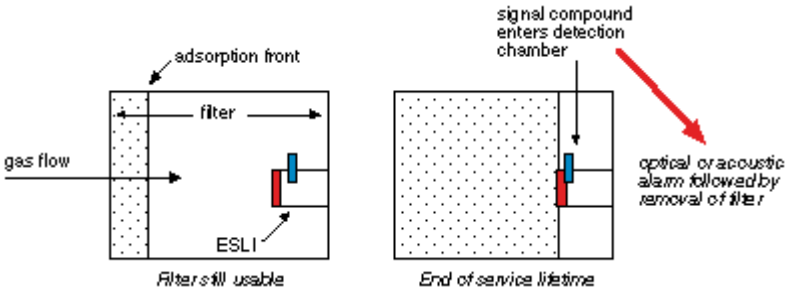

Figure 36: Schematic of TNO's optochemical sensor for detecting the release of a fluorescent indicator dye [112]

2.6 ESLIs for carbon adsorption beds.

The information presented in the earlier sections of this report was focused on ESLIs for respirator cartridges or canisters. Conversely, work on the residual life or the end of service life of filter beds should also be considered as potential applications for respirator cartridges. These methods are briefly discussed below.

In 1960, Philip [113] reported that the residual life of carbon adsorption beds could be determined by passing beta-radiation through the adsorption bed. Unfortunately, applying beta-radiation through a respirator cartridge while being worn is impractical and therefore this method cannot be considered as an ESLI.

In 1994, Martin Marietta Energy Systems patented [114] an apparatus and method for detecting chemical permeation of nerve, blister and toxic industrial chemicals, through protective clothing. The patent claims that phenanthrene (a strong luminescing compound) could be applied to detect permeation of hazardous chemicals (which do not luminesce) by measuring the reduction in luminescence. The major drawback to this design was the absence of an automatic warning device for notifying the user that chemical permeation had exceeded acceptable concentrations but instead concentrations could only be measured with a portable handheld luminescence monitor. In addition, a major concern is whether personal body odour permeation through clothing could also reduce the indicator's luminesce. Despite these concerns, this indicator system may have the potential to be integrated into a respirator ESLI system.

In the past decade, several patents have been awarded on determining the residual life of carbon-based filters by measuring the heat differentiation during gas adsorption/desorption [115, 116]. A similar method was applied by the American Optical Corporation in their 1979 respirator ESLI patent [82] (see Section 2.4, page 15 for discussion on the drawbacks in measuring adsorbent temperature changes for monitoring the life of a carbon filter). Unfortunately these procedures are only applicable to the laboratory where the rate of gas being fed through the carbon filter and the subsequent heat gains, can be carefully monitored. Consequently, these methods cannot be applied in the field; in particularly while the respirator cartridge is worn.

2.7 Conclusions

The complexity of implementing NIOSH's recommended cartridge change schedule [62] is best summarised by an official statement from AOSafety [117].

> " *There is no accurate, reliable method established, at this time, for determining service life of a cartridge for products that are a mixture of chemicals. It is a complex task that requires considerable professional judgement to create a reasonable change schedule. The change schedule for a mixture should be based on reasonable assumptions that include a margin of safety for the worker wearing the respirator. The best guesstimate can only be provided if the total concentration in the air is known. Without a known concentration, the service life of each substance identified in the MSDS, that is a liquid at room temperature, must be calculated at a determined concentration, which may not reflect the actual concentration of the contaminants in the air".*

Despite extensive work in the art of ESLIs for respirator cartridges, none of the designs encompass the capacity to simultaneously detect a range of CW agents (nerve/blister agents, acid gases eg HF, HCl etc) or hazardous toxic chemicals (hydrocarbon (eg benzene, toluene) or chlorinated hydrocarbon vapours (eg carbon tetrachloride)) (see Appendix, page 39). In recent years, significant innovative advancements in chemical micro-sensory technologies have transpired, with many of these new sensory systems potentially capable of concurrently detecting these hazardous agents inside the respirator cartridge. The second part in this series of reports will embark on evaluating the suitability of chemical micro-sensors towards respirator Active End of Service Life Indicators (AESLI). This evaluation will be aimed at providing the groundwork for the development of a respirator ESLI suitable for defence applications.

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Appendix A: Documented respirator ESLI mediums

Agents and type of indicator used on respirator cartridges for determining the end of service life of the unit.

Gas/agent	Indicator	Colour change	Reference
Ammonia	Red litmus	Red to blue	[39]
Hydrogen sulphide	Congo red soln.	Red to blue	[39]
Hydrochloric acid	Congo red soln.	Red to blue	[39]
Sulphur dioxide	Congo red soln.	Red to blue	[39]
Carbon monoxide	Palladium chloride	Brown-red to black	[39]
Vinyl chloride	Potassium permanganate	Purple to brown	[42, 45]
2-butanone	$Na_2Cr_2O_7$	Orange to dark green	[47]
1,1,1-trichloroethane	$Na_2Cr_2O_7$	Orange to dark green	[47]
Benzene	$Na_2Cr_2O_7$	Orange to dark green	[47]
SO_2	Indophenol	Dark blue to white	[52]
Chlorine	Indophenol	Dark blue to white	[52]
Chlorine	Benzoyl leuco methylene blue	White to blue	[52]
Acrylonitrile	Potassium permanganate	Purple to brown	[52]
Acetone	fibre optic chemical sensor	Decrease in light intensity	[95, 96]
Toluene	fibre optic chemical sensor	Decrease in light intensity	[95, 96]

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DSTO Defence Science and Technology Organisation
506 Lorimer St
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Respirator cartridges

19. ABSTRACT

One of the critical elements related to efficiency and safe use of respirator filter cartridges is their operational life span. Predicting the life span of a respirator cartridge is difficult because it is dependant on parameters such as environmental temperature, the nature and concentration of the contaminants and the rate of breathing. Ideally, respirator cartridges should include an End of Service Life Indicator (ESLI) system to warn the wearer when it is time to change cartridges.

The development of a cheap, reliable, disposable ESLI would significantly improve the protection of military units in a chemical warfare (CW) environment. Currently, no ESLI is available on the market that is capable of detecting a range of CW agents and toxic industrial chemicals (TICs) and therefore, the commercialisation potential of a successful ESLI is high. This report reviews all prior art relating to ESLIs for respirator cartridges which will provide the foundation for future development in this area.