

C.O.D 廢液之處理

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(一) 前言

C. O. D 為化驗室最常檢驗之水質項目，其檢驗完之廢液，因含有銀、汞、鉻……等離子，若任意排放而不加處理，將對環境造成極大之污染，且其廢液酸性極強，若不加以中和或稀釋，對污水廠機件及土木設施腐蝕性大。本文主要在探討如何在最經濟簡便之原則下，來回收或處理 C. O. D 廢液。

約略估計每作一個 C. O. D 水樣，於廢液中將含有銀離子 0.2g，汞離子 0.27g，若以每個工業區污水廠化驗室每天所作之水樣為 10 個，每月以 20 工作天計算，則每年每個工業區污水廠化驗室最保守的估計將有銀離子 480g（本廠實際產生 692g），及汞離子 648g（本廠實際產生 2.7kg）產生，若全省以 20 個工業區化驗室計算，每年工業區機構將有銀離子 9.6kg，汞離子 12.96kg 產生，若再加上全省一些私人機構、公家機構，及學術研究單位之化驗室，預估全省每年化驗室將有逾百 kg 之銀汞離子產生，若將這些廢液任意放流，對環境及人體健康之影響甚鉅。

(二) 銀及汞之毒性

銀 (Ag) 屬貴重金屬，能導致銀質沉著症，使皮膚及眼睛產生永久的藍灰色，0.4 至 1mg/l 的濃度即可使老鼠的腎、肝和脾發生病理變化。美國之飲用水標準，規定銀為 0 至 2μg/l。 $(1\mu\text{g}/\text{l} = \frac{1}{1000}\text{mg}/\text{l})$ 。

汞 (Hg) 俗稱水銀，在常溫下為唯一液態金屬，比重大 (13.6) 容易累積體內，造成水銀中毒。水俣病即是水銀中毒所致。由微生物分解為有機水銀（毒性較無機水銀大得多）蓄積在原體內，形成「食物鏈」，水銀一再被濃縮，最後危害到魚、鳥獸，甚至人類。水銀中毒為有機水銀刺激中樞神經發生中毒現象所造成，輕者全身倦怠、頭痛發汗、嘔吐，中毒者瞳孔縮小、言語障害、視力減退，重者意識失調、死亡等。

污水處理廠化驗室若將 C. O. D 廢液未經處理即放流至污水處理系統，雖可將之稀釋或部份分解，但亦會引起污水處理廠之一些週期性病變；而銀、汞經微生物之濃縮，將影響魚

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類、鳥獸，甚至人類之生存，實不可不慎。

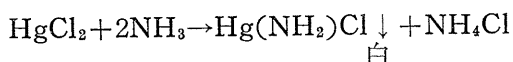
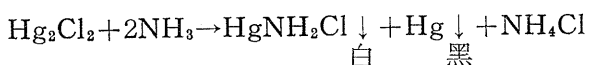
(三) C. O. D 廢液中銀、汞之處理回收

一、可回收氯化銀或純銀

於 C. O. D 廢液中加 NaCl 水溶液，則產生白色氯化銀沉澱。而 HgCl_2 及一些鐵、鉻離子均溶於水，經沉澱後即可將 AgCl 分離，充份水洗，使氯化銀溶於氨水，而 Hg_2Cl_2 與



HgCl_2 和 NH_4OH 作用均產生沉澱，過濾後溶液，加硝酸，再作氯化銀沉澱，充分水洗到硝酸銀消失，加熱烘乾，即得氯化銀。其加熱，過濾，洗滌宜於暗室或紅光下舉行。氯化銀可

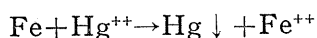


用於製金屬銀、照相術、鍍銀、醫療等用途。

若要精製純銀，則於上述步驟中，產生氯化銀沉澱後，充份水洗到硝酸銀消失，加精製的葡萄糖和苛性鈉加熱還原，以熱水充份洗滌生成泥狀銀泥，乾燥後，裝入純粹的生石灰坩堝溶解，即可將銀提煉出，若需更純之銀。則用電解精製，將氯化銀溶解，用電解法，可電解出純銀。

二、汞之回收

於上述步驟中，與 AgCl 分離後之水溶液，則含有汞離子，利用金屬之取代次序，將汞取出。



於含汞離子之溶液中投入鐵屑，經過長時間之取代反應，金屬汞則漸被析出，附着在鐵屑上，慢慢形成小圓球狀而沉降在底部，而部份鐵屑轉變為鐵離子。再利用鐵之沸點 2450°C 和汞沸點 357.33°C 之不同，而以減壓、蒸餾之使汞分離，即得汞，可用製汞鹽、溫度計、醫藥品、顏料、銀鏡、汞蒸多燈、汞劑，由礦中萃取金銀、理化儀器、催化劑、電解時之電權等。

若需精製則 (1) 通入空氣 1 ~ 2 小時，使不純物氧化。

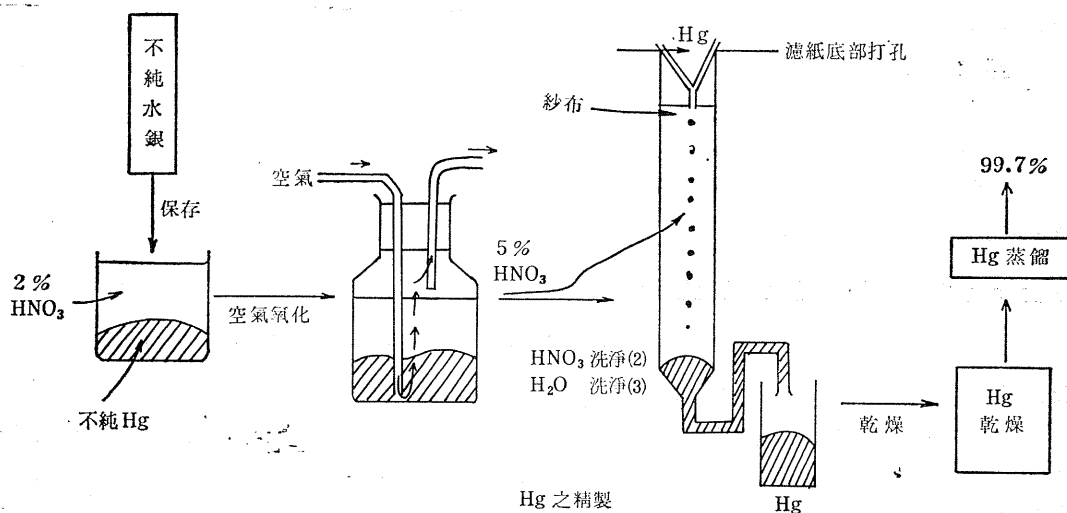
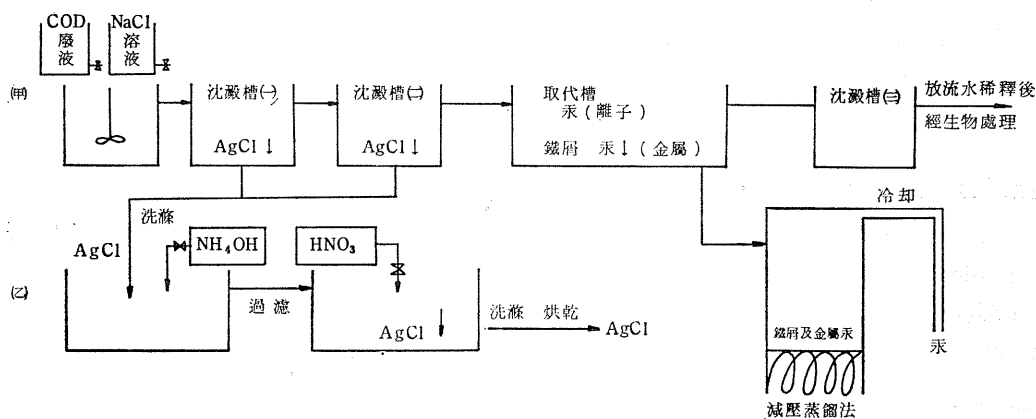
(2) 自 5 % HNO_3 洗滌塔頂滴下，重複操作 2 ~ 3 次，充份溶解不純物。

(3) 以水代替前項洗滌塔中之 HNO_3 ，重複洗滌至無酸性。

(4) 以分液漏斗分離水份，並用濾紙吸收水銀表面之水分後，置於乾燥器內乾燥之。

(5) 用減壓蒸餾法蒸餾之。因汞有毒不可以手觸摸。常濕下亦具有相當大的蒸氣壓，故須使實驗室通風良好。

(四) C. O. D 廢液中銀、汞之回收流程裝置



本回收處理設備分(甲)(乙)兩部份；因每日每個化驗室所生之 C. O. D 廢液有限，可用(甲)設備，讓粗製之 AgCl 及鐵屑和金屬汞積沉一定量（經幾個月後），再做一次 AgCl 、及 Hg 之精製處理。（流程乙）。亦可固定時間，再收集各工業區化驗室，或別機構化驗室之粗製 AgCl 及鐵屑、金屬汞，集中一起精製，則可省去麻煩。

(五) 檢 驗

爲了解處理流程中 C. O. D 廢液中所含之銀、汞離子處理情形，於流程操作上可用較簡單之方法檢驗，即在 AgCl 沉澱後之沉澱槽中，取上層液一滴添加一滴 0.1FKI，如無淺黃

色沉澱產生，即證明已無 Ag^+ 存在。在取代槽後之沉澱槽取上層液三滴，添加二滴 SnCl_2 溶液，若無白色或灰色沉澱產生，可確認無 Hg_2^{++} 存在。同樣再取上層液數滴，添加 NH_4OH ，如無白色沉澱 $\text{Hg}(\text{NH}_2)\text{Cl}$ ，即表示無 HgCl_2 存在。

如必要檢驗放流水之汞及銀離子，則依下列方法行之。

Silver

Qualitative analysis

10 ml of the water sample is treated in a test-tube with a few drops of Feigl's reagent, 5 ml diethyl ether superimposed, and the mixture shaken. In the presence of silver ions a reddish-brown film forms at the interface between the two phases. Lower limit of detection: about 0.4mg/l.

Reagent preparation

Feigl's reagent: Dissolve 0.03g 5-(4-Dimethylaminobenzylidene) rhodanine GR in 100 ml Acetone GR.

Reagents

Cat. No.	Packages
14 Acetone GR	1l, 2 $\frac{1}{2}$ l
921 Diethyl ether GR	1l, 5l
3059 5-(4-Dimethylaminobenzylidene) rhodanine GR (reagent for silver).....	5g

Quantitative analysis

Photometrically with dithizone

Suitable for determination of silver ions in concentrations from 0.05 to 1.50mg Ag^+/l .

Interferences and pre-treatment

In order to achieve satisfactory results of measurement, all the apparatus should be cleaned extremely carefully before the determination by subjecting it to the action of Extran solution for one to two hours, and then rinsing successively with deionised water, dithizone solution, carbon tetrachloride and double-distilled water. To test for cleanness, 20 ml double-distilled water is introduced into the separating funnels before each determination, adjusted to pH about 9.5 with 1-2 drops of ammonia solution (0.91), and 0.5 ml dithizone solution added. After vigorous shaking for one minute the carbon tetrachloride phase should be colourless.

Interferences by zinc, cadmium and nickel ions in higher concentrations ($>100 \text{ mg/l}$) and by copper ions are eliminated by addition of 2 ml Titriplex III solution per sample volume.

In the presence of sulfide ions the sample is evaporated to dryness on a water bath with 1 ml nitric acid (about 1.40). The residue is moistened with 2 ml nitric acid (about

1.40), evaporated to dryness once again, and taken up in 50 ml doubledistilled water, with heating.

The interference of organic substances and iron (III) ions is excluded by addition of hydroxylammonium chloride solution; this method is not applicable to solutions acidified with nitric acid. Larger amounts of organic constituents (potassium permanganate-consuming capacity >25 mg/l) are decomposed by evaporation with sulfuric acid (about 1.55) and a few drops of nitric acid (about 1.40).

Procedure

Extreme care, and cleanness of apparatus, is necessary to avoid interferences; the determinations should always be carried out with the same cleaned apparatus.

Treat 100 ml test water in a 250 ml separating funnel with 15 ml nitric acid (about 1.035) or sulfuric acid (about 1.05), then with 50.0 ml dithizone solution, and shake vigorously for 5 min. If the carbon tetrachloride phase develops a golden yellow colour, a smaller starting volume of the test water should be taken. After complete separation of the phases, run the organic extract into a second separating funnel, treat with 10 ml ammonia solution (about 0.98), and shake for 2 min in a shaking machine. Dry the outlet tube of the separating funnel with a small roll of filter paper. Then allow some of the organic phase to run out in order to rinse the outlet tube. Filter the carbon tetrachloride layer through a plaited filter into a 1-cm cell, and measure at 470 nm (e.g., in an ELKO II. or III with Filter S 47 E) against a blank treated in the same manner.

The reference curve is prepared from standard solutions of silver nitrate treated in the same manner as the water sample.

Calculation

The starting volume of the test water is to be taken into account in calculating the silver ion content in mg Ag^+ /l.

1 meq silver ions $\triangleq 107.88$ mg Ag^+

Reporting of results

The values are rounded off to 0.01 mg/l for a silver ion content of less than 1 mg/l, and to 0.1 mg/l for 1 mg/l or more.

Reagent preparations

All the solutions are prepared with double-distilled water.

Ammonia solution (about 0.98): Mix 110 ml Ammonia solution min. 25% (0.91) Suprapur with 400 ml double-distilled water.

Dithizone solution: Dissolve about 12–13 mg Dithizone (1,5-diphenylthiocarbazon) GR in 100 ml Carbon tetrachloride GR (for determinations with dithizone). —Dilute 10 ml of this stock solution with 100 ml Carbon tetrachloride GR (for determinations with dithizone). Only stable for about 1 day! —Store the solutions in brown bottles.

Extran solution: 2% aqueous solution of Extran MA 01 alkaline.

Hydroxylammonium chloride solution: Dissolve 20g Hydroxylammonium chloride GR in 100 ml double-distilled water. The solution is stable for about 1 week. Nitric acid (about 1.035): Mix 580 ml double-distilled water with 50 ml Nitric acid min. 65% (about 1.40) tested by the dithizone method GR.

Sulfuric acid (about 1.55): Carefully pour 350 ml Sulfuric acid 95-97% (about 1.84) GR into 310 ml double-distilled water.

Sulfuric acid (about 1.05): Mix 440 ml double-distilled water with 22 ml Sulfuric acid 95-97% (about 1.84) GR.

Silver standard solution: Treat 1.5746g Silver nitrate GR with 10 ml nitric acid (1.035), and make up to 1000 ml with double-distilled water. 1 ml \triangleq 1 mg Ag⁺. or:

Treat 1.4453 g Silver sulfate GR with 10 ml sulfuric acid (1.05), and make up to 1000 ml with double-distilled water. 1 ml \triangleq 1mg Ag⁺.

The dilution solutions necessary for plotting of the reference curve are freshly prepared from one of these solutions.

Titriplex III solution: Dissolve 5 g Titriplex III GR in double-distilled water to make 100 ml.

Reagents

Cat. No.	Packages
9532 Alkalit [®] indicator strips pH 7.5-14.0 non-bleeding graduated in 0.5 pH units	1 pack
5428 Ammonia solution min. 25% (0.91) Suprapur [®]	250 ml, 1 l
3092 Dithizone (1,5-diphenylthiocarbazone GR	5 g, 25 g, 100 g
7555 Extran [®] MA 01 alkaline	1 l, 5 l
4616 Hydroxylammonium chloride GR	100 g, 250 g, 1 kg
456 Nitric acid min. 65% (about 1.40) tested by the dithizone method GR	1 l, 2 1/2 l
731 Sulfuric acid 95-97% (about 1.84) GR	1 l, 2 1/2 l
1512 Silver nitrate GR	25 g, 100 g, 250 g, 1 kg
1509 Silver sulfate GR	25 g, 100 g
2208 Carbon tetrachloride GR (for determinations with dithizone)	1 l, 2 1/2 l
8418 Titriplex [®] III [(ethylenedinitrilo) tetraacetic acid disodium salt] (dihydrate) GR	100 g, 250 g, 1 kg, 5 kg

Mercury

Quantitative analysis

Photometrically with dithizone

Suitable for determination of mercury ions in concentrations between 0.01 and 2.0 mg Hg^{2+} /l.

Interferences and pre-treatment

Silver, gold, palladium and platinum ions interfere at all concentrations.

The interference of larger concentrations of copper ($\text{Cu} : \text{Hg} > 10^3$) is eliminated as described under Procedure.

For determination of the total mercury organically bound mercury must be mineralised before the quantitative estimation, and the volatility of most mercury compounds must be borne in mind: Boil 100 ml of the water sample for 2h under reflux with 10 ml sulfuric acid (about 1.84) and sufficient potassium permanganate solution to leave a slight violet colouration at the end of the oxidation process. After cooling, decolourise, or dissolve precipitated manganese oxide, with a slight excess of hydroxylammonium chloride solution, boil, and cool to room-temperature.

Since mercury ions have a great tendency to adsorption, all glass apparatus should be carefully rinsed with dilute nitric acid, and then deionised water, before use.

Procedure

Introduce 100 ml, or a smaller volume made up to 100 ml with deionised water, of the original water sample acidified with 1 N sulfuric acid to pH 0-1, or 100 ml of the sample pre-treated as necessary, into a separating funnel, and extract with two 10.0-ml portions of dithizone solution. The last extract must remain green; if not, a smaller volume of the water made up to 100 ml with deionised water should be used.

If the water sample contains larger amounts of copper ($\text{Cu} : \text{Hg} > 10^3$), extract fractionally in the separating funnel as often as is required for the pure violet colour of copper dithizonate to appear. Shake the combined organic extracts twice for 2 min in each case with 15 ml 1 N sulfuric acid and 1 ml potassium permanganate solution. The mercury goes into the aqueous phase, which is decolourised with a few drops of hydroxylammonium chloride solution. Now extract the aqueous phase with two 10.0 ml portions of dithizone solution.

Wash the combined organic extracts (from the treatment described in paras. 1 and/or 2) free from dithizone with three 10-ml portions of dilute ammonia solution, and then desensitise by shaking vigorously with 10 ml dilute acetic acid. After separation of the phases, drain the organic phase through a filter paper into a 2-cm cell, cover the cell immediately, and measure at 485 nm (e.g., in an ELKO II or III with Filter S 49 E)

against a blank treated in the same manner. The reference curve is prepared from standard solutions of mercury (II) chloride or dilution solutions of Mercury standard solution Titrisol treated in the same manner as the water sample.

Calculation

Any dilution of the water sample to 100 ml starting volume is to be taken into account in the calculation.

Reporting of results

The values are rounded off to 0.01 mg/l.

1 meq mercury(II) ions \triangleq 100.30 mg Hg²⁺.

Reagent preparations

Ammonia solution, dilute: Dilute 5 ml Ammonia solution min. 25% (0.91) GR to 1000 ml with deionised water.

Dithizone solution: Dissolve 0.02g Dithizone GR by shaking for a longish period in 100 ml Carbon tetrachloride GR (for determinations with dithizone), and then extract with four 50-ml portions of dilute ammonia solution.

Filter the combined aqueous extracts through a plaited filter, add 100 ml Carbon tetrachloride GR and 1 ml Hydrochloric acid min. 25% (about 1.125), and shake immediately. Wash the green organic phase with three 50 ml portions of deionised water, and filter again. The solution is stable for about 4 weeks.

For the analysis a dilute solution of dithizone is employed which should be freshly prepared before use in each case: Make 10 ml of the dithizone stock solution up to 200 ml with Carbon tetrachloride GR.

Acetic acid, dilute: Dilute 15 ml Acetic acid glacial min. 96% (about 1.06) GR to 100 ml with deionised water.

Hydroxylammonium chloride solution: Dissolve 20 g Hydroxylammonium chloride GR in deionised water to make 100 ml.

Potassium permanganate solution: Saturated solution at room temperature (about 6 g Potassium permanganate GR in 100 ml deionised water).

Mercury standard solution: Dissolve 1.354 g Mercury (II) chloride GR in 1 N Sulfuric acid to make 1000 ml. 1 ml \triangleq 1 mg Hg²⁺.

For preparation of the reference curve fresh dilutions of this solution are made with 1 N Sulfuric acid as required.

The Mercury standard solution Titrisol can also be used in a similar manner. Nitric acid, dilute: Mix 100 ml Nitric acid min. 65% (about 1.40) tested by the dithizone method GR with 300 ml deionised water.

Reagents

Cat. No.	Packages
5432 Ammonia solution min. 25% (0.91) GR	1 l, 2½ l, 5 l

3092	Dithizone (1,5-diphenylthiocarbazone) GR.....	5 g, 25 g, 100 g
62	Acetic acid glacial min. 96% (about 1.06) GR	1 l, 2 ¹ / ₂ l
4619	Hydroxylammonium chloride (max. 0.000001% Hg) GR.....	250 g
5084	Potassium permanganate (max. 0.000005% Hg) GR	1 kg
4419	Mercury (II) chloride GR	50 g, 250 g, 1 kg
9916	Mercury standard solution Titrisol [®] 1.000 g \pm 0.002 g Hg [Hg (NO ₃) ₂ in dil. nitric acid]	1 amp.
456	Nitric acid min. 65% (about 1.40) GR	1 l, 2 ¹ / ₂ l
316	Hydrochloric acid min. 25% (about 1.125) GR	1 l, 2 ¹ / ₂ l
732	Sulfuric acid 95-97% (about 1.84) (max. 0.0000005% Hg) GR	2 ¹ / ₂ l
9072	1 N Sulfuric acid.....	1 l, 5 l
9981	1N Sulfuric acid Titrisol [®] concentrated solution for preparation of 1 litre of 1 N solution.....	1 amp.
9540	Special indicator strips pH 0-2.5 non-bleeding graduated in 0.5 pH units	1 pack
2208	Carbon tetrachloride GR (for determinations with dithizone).....	1 l, 2 ¹ / ₂ l

(六) 處理後 C. O. D 廢液放流水之處理

處理後 C. O. D 廢液中，因鐵屑之取代作用，致使放流水中含有鐵離子、鉻離子（原本廢液中即有）。且酸性仍然極強，足以腐蝕機件、土木措施，仍必須作稀釋或中和，因顧及經濟及鹽泥之處理問題，乃以本廠每日 3500m³ 之水量來稀釋，而將鐵離子，作為生物處理微生物之養份。（理論上 BOD:N:P:Fe=100:5:1:0.5）。鉻離子含量微少，經稀釋後應無多大影響，但仍有再檢討之必要。

(七) 與傳統式處理方法比較

一般去除廢水中銀離子，係使生成 Ag₂S 或 AgCl 沉澱，但仍以回收銀，或是作成更有用之藥品才是優良之方法。

汞離子一般用凝結沉澱法或離子交換樹脂法，但這二種方法處理後之沉澱物，均須要作處理，或固化。在經濟上及處理程序上較不方便。而回收金屬汞再利用才是最好之方法。

(八) 結 語

以全省化驗室所檢驗 C.O.D 項目中為例，每年將產生極為驚人之 Ag、Hg 離子，若不加以處理，任意放流，雖然現在不易發現禍害徵兆，但在百年千年之後，所累積 Ag、Hg 之毒性濃縮，或經生物分解成有機汞，則對後代子孫有很不良之影響。雖然我們現在所做的只

是舉手之勞，但給後代的受益將是無窮。日本對化驗室所產生之污染（毒性物質）非常重視，管制相當嚴格。化驗室所產生之廢液不得任意放流，必須收集另外處理，如化驗人員不注意將廢液傾倒入排放系統，則警報器將大響。由此可看出日本人對公害之重視，且汞屬於毒性高、頑強、及生物蓄積之物質，若不加管制，而任其放流，所造成之禍害，是不可言喻。何況，歐市於1976年5月4日公布危險性與毒性物質排入水域環境造成污染之指令（directive）。將毒性物質依據其毒性程度之不同區分為二大類：一為黑名單（black list），一為灰名單（grey list）。而汞及銀分別列於黑、灰名單之中。所幸，當筆者寫作本文時，立法院已三讀通過毒性物質管制辦法，此乃一極明智之作法。亦希望各有關主管機構能儘速訂定細則辦法，使毒性物質管制納入軌道，並將使用過程中所產生之毒害物質，明確訂定管制辦法，以減少公害對人體健康之危害，並確保優良之環境品質。